REVIEW ARTICLE

STRENGTH, TOUGHNESS AND THERMAL SHOCK RESISTANCE OF ANCIENT CERAMICS, AND THEIR INFLUENCE ON TECHNOLOGICAL CHOICE*

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The basic underlying theory for the strength, toughness and thermal shock resistance of brittle multiphase clay ceramics, together with the measurement procedures to determine these parameters, are first outlined. Published experimental data obtained for test bars containing different types of temper and fired to a range of temperatures are then compared both with theoretical predictions and between themselves. The results confirm that to produce pottery with high strength requires high firing temperatures and low temper concentrations. Conversely, to produce pottery with high toughness and thermal shock resistance requires low firing temperatures and high temper concentrations, with platy or fibrous temper being most effective. There is no convincing published evidence that strength and toughness requirements were a significant factor in determining the technological choices (clay type, temper type and concentration, and firing temperature) in the production of pottery used as containers for transport and storage. In contrast, the routine use of high temper concentrations and low firing temperatures in the production of cooking pots suggests that the requirement for high thermal shock resistance was a factor that at least influenced technological choice in this case. In addition, there is some evidence that limestone and shell were, on occasions, deliberately chosen as temper in cooking pots. The need to take into account the crucial role that the full range of environmental, technological, economic, social, political and ideological factors have in influencing technological choice is also emphasized. This review highlights the fact that our current understanding of the factors determining strength, toughness and thermal shock resistance of clay ceramics is still far from complete. Further systematic measurements of these parameters, together with the establishment of a systematic database of the range of technological choices associated with the production of cooking pots, are therefore to be encouraged.

INTRODUCTION

Two aspects of the performance characteristics of pottery vessels in use are the primary concern of this paper: first, they must be able to retain their contents; and, second, they must survive impact and a rapid change in temperature without cracking. The ability of pottery vessels to retain their contents is dependent on their withstanding a sustained load or stress, and is therefore determined by their fracture strength or modulus of rupture. In contrast, the ability of vessels to survive impact or a rapid change in temperature is dependent on their withstanding a short-term load or stress, and is therefore dependent on their toughness and thermal shock resistance. In the case of thermal shock, the stresses driving fracture are in turn dependent on the thermal expansion and thermal conductivity of the pottery walls.

The primary aim of this review paper is to provide an outline of the underlying theory for the strength, toughness and thermal shock resistance of clay ceramics, together with a summary of the procedures used for measurement and a critical survey of published experimental data on these parameters. Subsequently, on the basis of published work on archaeological and ethnographic ceramics, an attempt is made to assess the extent to which the choice of clay, temper and firing temperature employed in production might have been influenced by the mechanical and thermal properties required in use.

Shepard (1956), in her ground-breaking book *Ceramics for the archaeologist*, provides probably the first experimental data for and discussion of the potential importance of the tensile strength of archaeological ceramics. However, it is the seminal paper by Braun (1983), entitled 'Pots as tools', that represents the first serious attempt to explain observed changes in technological choice in production in terms of the changing performance characteristics required in use. Subsequently, Steponaitis (1983, 1984) measured the tensile strength and Young's modulus for Mississipian period shell-tempered pottery from North America and used these data to estimate thermal shock resistance. Conversely, Woods (1986) argued strongly that the emphasis given to the role of the mechanical and thermal properties in determining the technological choices made in production was not justified. However, in North America in particular, this interrelationship between physical properties and technological choice continued to be assessed in a series of papers published over the next 10 years or so.

Bronitsky (1986) provided a comprehensive review of the physical properties of ceramics and the methods by which they could be measured. Bronitsky and Hamer (1986), Feathers (1989), Feathers and Scott (1989), West (1992) and Hoard *et al.* (1995) all provided experimental data for the strength, toughness and, in some cases, thermal shock resistance of low-fired pottery tempered mainly with quartz sand, limestone and shell. In part because of the probability of alteration in strength and toughness during both use and subsequent burial, these measurements were made on replicate test pieces rather than on the archaeological sherds themselves. In addition, Skibo *et al.* (1989) provided an overall assessment of the mechanical and thermal properties, and the performance characteristics of organic-tempered pottery, and Schiffer *et al.* (1994) considered the interrelationship between surface treatment and the thermal response of cooking pots. Neupert (1993, 1994, 1995) developed a method for the direct measurement of the strength of pottery sherds and published strength data for a range of archaeological pottery from North America. Finally, Kilikoglou *et al.* (1995, 1998) provided a comprehensive set of strength and toughness data for high-fired calcareous clays tempered with quartz sand, in replication of Bronze Age pottery from the Mediterranean.

STRENGTH AND TOUGHNESS

Theoretical considerations

Fracture strength (σ_f) is the maximum stress at the point of failure during loading. It is not an intrinsic property of a material but depends greatly on the concentration and size of any cracks or flaws, since these act as stress concentrators. In the case of tension or bending, as compared to compression, the stress (σ_m) in the vicinity of a crack is given by

$$\sigma_m = 2\sigma(c/\rho)^{1/2},$$

where σ is the applied stress, c is the half-length of the crack and ρ is the radius of the crack tip, which is typically of the order of the interatomic spacing. Therefore, under an applied stress, a crack starts to propagate when the stress concentrated at the crack tip (σ_m) is sufficient to break atomic bonds. As the length of the crack increases, the stress concentrated at the crack tip also increases, so that the crack can continue to propagate under a progressively reduced applied stress.

However, the preferred approach to understanding fracture strength and toughness is to follow that of Griffith, and consider the energy balance between stored elastic energy and the surface energy of the crack (Kingery *et al.* 1976, 783; Lawn 1993). Thus, again in the case of tension or bending, the total energy (W) associated with a crack of length $2c$ in a thin plate is given by

$$W = -\pi c^2 \sigma^2/E + 2cG_c,$$

where E is Young's modulus and G_c is the surface energy of the two newly created crack surfaces. G_c, which provides a measure of the toughness, is also sometimes referred to as the intrinsic fracture energy; that is, the energy expended in breaking atomic bonds. Crack propagation starts to occur when the decrease in stored elastic energy associated with its extension equals the increase in surface energy associated with the formation of new surfaces, the condition for this being $dW/dc = 0$. Therefore, the fracture strength is given by

$$\sigma_f^2 = G_c E/\pi c. \tag{1}$$

For this applied stress the system is unstable in that, with increasing crack length, the decrease in stored elastic energy exceeds the increase in the surface energy. Therefore, the crack propagates spontaneously without limit, resulting in complete failure, any excess elastic energy being transformed into the kinetic energy of the moving crack.

For multiphase clay ceramics, consisting of non-plastic inclusions (i.e., both added temper and indigenous inclusions) in a clay matrix, the situation is more complex. In this case, fracture normally occurs through the clay matrix. Therefore, the intrinsic fracture energy (G_c) and, thus, the fracture strength (σ_f) are dependent on both the original particle size and packing of the clay particles, and on the vitrification properties of the clay and the firing temperatures used in the production of the ceramic. For low firing temperatures, intrinsic fracture energy and fracture strength depend on the strength of bonding at the interfaces between the clay particles. The strength of this bonding increases with increasing firing temperature, as the vitrification—and hence the fusion—between the particles increase, the extent of vitrification for a particular firing temperature being dependent on the type of clay used. Ultimately, the extent of the vitrification of the clay is such as to form an essentially continuous glassy matrix, in which case intrinsic fracture energy and fracture strength depend on the strength of the atomic bonds within this matrix.

The presence of added temper particles results in significantly greater energy dissipation during crack propagation as compared to that associated with unstable crack propagation in a homogeneous clay matrix. This additional energy dissipation is due to a combination of crack deflection and bifurcation at the interfaces between the temper particles and clay matrix; fracture of temper particles or friction associated with pulling temper particles out from the clay matrix; and crack arrest at pores. Thus, the total fracture energy (G) during crack propagation in a clay ceramic containing temper is the sum of (1) the intrinsic fracture energy (G_c) and (2) the additional energy dissipated during crack propagation (G_t). This latter is the result of crack deflection, bifurcation and arrest, as well as fracture of the temper particles or their being pulled out from the clay matrix. Because of the significantly greater dissipation of energy during crack propagation in such ceramics, the crack once initiated is arrested rapidly and a further input of energy is necessary in order for crack propagation, which is now stable, or at least semi-stable, to continue. As a result, the toughness of a ceramic containing added temper, which is determined by the total fracture energy ($G_c + G_t$), is higher than that of a ceramic with a homogeneous clay matrix, which is determined by the intrinsic fracture energy (G_c) alone.

However, it must be emphasized that the toughness of a ceramic containing temper also depends critically on the firing temperature used in its production. For the high-fired ceramics, cracks involve the breaking of atomic bonds and are therefore initiated at fairly high stresses. Because the stored energy is high, such cracks travel fast and unstably, and energy dissipation during crack propagation is inefficient and may not be sufficient to arrest the crack. In contrast, for low-fired ceramics, cracks involve the separation of clay platelets and are therefore initiated at low stresses. As a result, higher energy dissipation occurs during crack propagation and crack arrest is easier.

Finally, for multiphase clay ceramics, it should be noted that Young's modulus (E) is essentially the sum of the products of the moduli of the individual phases with their associated volume fractions, and that an important phase to include is pore space, which has an approximately zero Young's modulus. For spherical pores or non-contacting spherical inclusions, Young's modulus for multiphase materials under tension is given by

$$E = E_0(1 - 1.9V_f + 0.9V_f^2),$$

where E_0 is the modulus of the solid non-porous matrix and V_f is the volume fraction of pores.

Measurement procedures

In measuring fracture strength, it is important to distinguish between the strength of the material from which a pottery vessel is made and the actual 'failure limit' of the vessel as a whole, which is also dependent on the shape of the vessel, the thickness of its walls, the method of manufacture and the loading method in use. This distinction can result in a conundrum, in that the thicker a vessel wall, the greater will be the net strength. However, because the largest or sharpest flaw is responsible for fracture under tensile strength, a thicker vessel wall will increase the probability that a critical flaw, leading to unstable failure, will be present.

Because the strength of ceramic materials is so very dependent on the flaw content, repeat strength measurements can give highly variable results, which can only be treated using the so-called Weibull (weak-link) statistical method (Ashby and Jones 1996b, 178). Also, because of the dependence of strength on the dimensions of the specimen and the loading method, it is important to know these parameters when comparing strength measurements, and only to compare measurements made on specimens with similar dimensions and using similar loading methods.
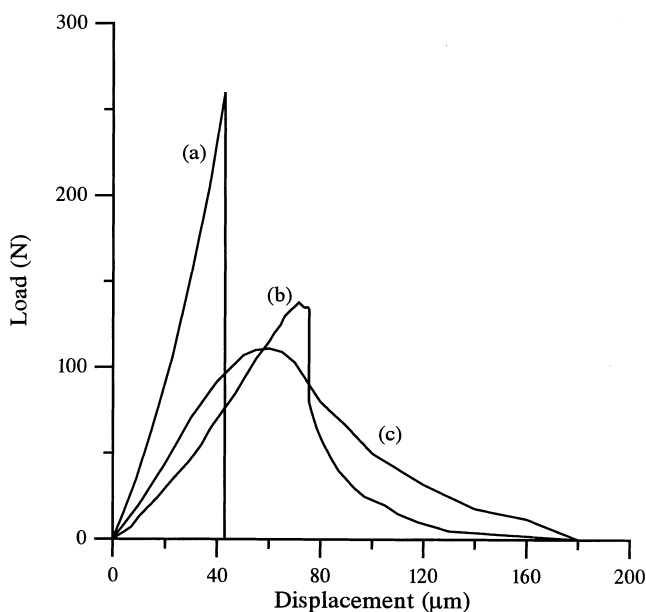
Figure 1 *Typical uncorrected load–displacement curves for different types of fracture: (a) unstable; (b) semi-stable; (c) stable.*

Fracture strength (σ_f) is usually determined as the transverse rupture strength (TRS) or modulus of rupture (MOR), from a three- or four-point bend test on a bar (typically 10 mm × 20 mm cross-section and 100 mm length) that does not have any notch cut in it. As an alternative, Neupert (1994) has developed a ball-on-three-ball tester that is particularly suitable for measurements on irregularly shaped, curved archaeological sherds. Similarly, Vekinis and Kilikoglou (1998) have shown that Hertzian point loading tests, undertaken on small disc-shaped specimens (typically 25 mm in diameter and 10 mm thick) cut from sherds, also provide valid estimates of fracture strength.

The intrinsic fracture and total fracture energies (G_c and ($G_c + G_t$) respectively) are usually determined from a three- or four-point bend test on a notched bar, the notch of known dimensions cut into the underside of the bar providing the largest flaw at which the crack is initiated. For unstable fracture, complete failure occurs at maximum load, with the load dropping immediately to zero: a typical load–displacement curve is shown in Figure 1 (a). For semi-stable fracture, the load drops sharply on initial failure, but the crack is rapidly arrested and thereafter the load necessary for continued displacement decreases gradually until final failure: a typical load–displacement curve is shown in Figure 1 (b). Finally, for completely stable fracture, the crack is immediately arrested and the load decreases gradually from maximum load until final failure, as shown in Figure 1 (c). In the context of clay ceramics, unstable fracture is typically associated with high-fired porcelain, semi-stable fracture with standard earthenware, and stable fracture with low-fired, coarse-tempered earthenware.

The area under the rising linear part of the load–displacement curve, after correction for the compliance of the testing machine materials, provides a measure of the stored elastic energy at the moment of fracture. However, for unstable and semi-stable crack propagation, a proportion of this stored energy will have been transformed into kinetic energy. Therefore, this area does

not provide the correct value for the intrinsic fracture energy (G_c). Instead, intrinsic fracture energy (G_c) must be calculated using equation (1), with the fracture strength (σ_f) and Young's modulus (E) being determined from the gradient of the linear part of the load–displacement curve just before failure, again after correction for the compliance of the testing machine materials. For semi-stable fracture, the tail of the load–displacement curve provides a measure of the energy dissipated during crack propagation (G_t) as a result of crack deflection, bifurcation and arrest, and the temper fracture or pull out. For stable fracture, in which none of the stored energy is transformed into kinetic energy, G_c and G_t are given, respectively, by the areas under the rising linear part and the tail of the load–displacement curve.

In using a notched bar in the estimation of the total fracture energy of multiphase, clay ceramics, the measurements must be made under carefully controlled conditions. First, the notch must leave sufficient of the cross-section of the bar uncut so that the area of the final fracture surface is sufficiently large in comparison with the dimensions of the temper particles. Otherwise, the energy dissipation resulting from crack deflection, bifurcation and arrest, and temper fracture or pull out, will not be fully represented. Second, the rate at which the bar is loaded (normally 50–100 μm min^{-1}) must be sufficiently slow to allow the system time to absorb the energy offered to it and thus ensure stable crack propagation.

An alternative approach is to measure the energy required to break a test specimen in a single blow from either a pendulum or a falling weight (Bronitsky 1986). With this method, the load is applied very rapidly to an essentially point area on the test specimen and, as a result, there will be insufficient time for the system to absorb the energy offered to it. The parameter thus measured is the energy dissipation under impact, and this is not the same as toughness under slow constant loading, the energy dissipation during crack propagation following impact being very small. In fact, it is possible that a specimen with low strength exhibits the lowest impact toughness, opposite to what is found during slow loading.

A further alternative, requiring only small disc-shaped specimens, is to measure the abrasion wear resistance (Vekinis and Kilikoglou 1998). This approach is based on the assumption that if a brittle material is indented at a sufficiently high load by a sharp indentor, such as a sharp silicon carbide particle, an elastic–plastic stress field is generated, leading to extensive lateral microcracking, which is the predominant material removal process for ceramics. Lateral cracks form once a critical load has been exceeded and it can be shown that this load is proportional to the fourth power of the fracture toughness and inversely proportional to the third power of hardness of the material. Therefore, abrasion wear resistance gives an indirect, non-standard measurement of total fracture energy and is very dependent on the conditions employed in the tests.

In interpreting fracture strength and toughness measurements for ceramic materials, it is important to remember that, because these parameters are highly dependent on the flaw content, their distribution and nature, the results are very sensitive to material preparation and test specimen geometry. Special care must be taken to avoid a concentration of large flaws in the test specimens that are unrepresentative of the normal population, since cracks are usually initiated at such flaws. When this occurs, the value measured will be much lower than those for other specimens from the same series and the results should be treated with caution. In consequence, measurement of multiple specimens from each series is essential in order to obtain statistically valid results. Also, the clays used should be fine-grained (at least below silt level) in order that they are rich in the clay minerals and thus ensure a detectable effect on mechanical performance with only small additions of temper. In preparing the test specimens, special care must be taken to produce blunt edges in order to avoid stress concentrations. In addition, since the testing

Table 1 *A summary of experimental procedures*

	1*	2	3/3A	4
Type of clay	Highly calcareous	Non-calcareous	Non-calcareous	Non-calcareous
Firing temperature (°C)	950 (800, 1100)	600	600	700
Tempering materials	Quartz	Quartz, grog, limestone	Quartz, shell	Quartz, grog, shell, mica, wollastonite
Proportions (%)	0, 5, 10, 20, 40	35	25, 45	0, 20, 40
Test bar size (mm)	$10 \times 10 \times 70$	$12 \times 12 \times 124$	$12 \times 12 \times 124$	$12 \times 18 \times 80$
TRS	Three-point, unnotched	Three-point, unnotched	Three-point, unnotched	Three-point, unnotched
Fracture energy	Four-point, notched	Three-point, unnotched	Three-point, notched	Three-point, notched
Loading rate (μm min^{-1})	50	100	100	
Intrinsic†	Calculated	Area	Calculated	Area
Propagation‡	Area	Area	Area	Area

* Sources: 1, Kilikoglou *et al.* (1995, 1998); 2, Hoard *et al.* (1995); 3, Feathers (1989); 3A, Feathers and Scott (1989); 4, West (1992).

† Intrinsic fracture energy (G_c) either calculated using the relationship given in equation (1) or determined from the area under the rising part of the load–displacement curve.

‡ Crack propagation energy (G_t) determined from the area under the 'tail' of the load–displacement curve after initial failure.

frames used for bending and compression slide in a parallel mode, the surfaces of the test specimens should be parallel.

Quartz temper

A comprehensive set of strength and toughness measurements relevant to ancient ceramics are those undertaken by Kilikoglou and his colleagues (Kilikoglou *et al.* 1995, 1998) on test bars made from a calcareous clay tempered with varying concentrations of naturally weathered (and therefore rounded) quartz sand and fired at 950°C (Fig. 2 and Table 1). They have shown that low concentrations of quartz temper (up to about 10% by volume) result in unstable brittle fracture with high fracture strength but no crack propagation energy contribution (G_t) to the total fracture energy, and thus to toughness. Conversely, high concentrations of quartz temper (20% and above) result in semi-stable fracture with lower fracture strength but a significant crack propagation energy (G_t) contribution to the total fracture energy, and thus to toughness. Furthermore, in addition to decreasing with increasing concentration of quartz temper, the fracture strength also decreases as the diameter of the temper particles is increased from 100 μm to 750 μm, the decrease being particularly pronounced for temper concentrations of less than about 20%. In contrast, the dependence of the total fracture energy on temper size is much less pronounced.

The explanation proposed for the observed differences in fracture properties with concentration of quartz temper is that differential shrinkage or expansion of the clay and quartz inclusions during drying, firing and subsequent cooling resulted in the formation of a network of microcracks, as well as in debonding between the quartz inclusions and the clay matrix. During drying, the clay matrix contracts and exerts a hydrostatic compressive stress on the quartz inclusions, resulting in matrix microdamage in the vicinity of the inclusions. During subsequent firing, the large expansion that accompanies the α–β phase transition in quartz at
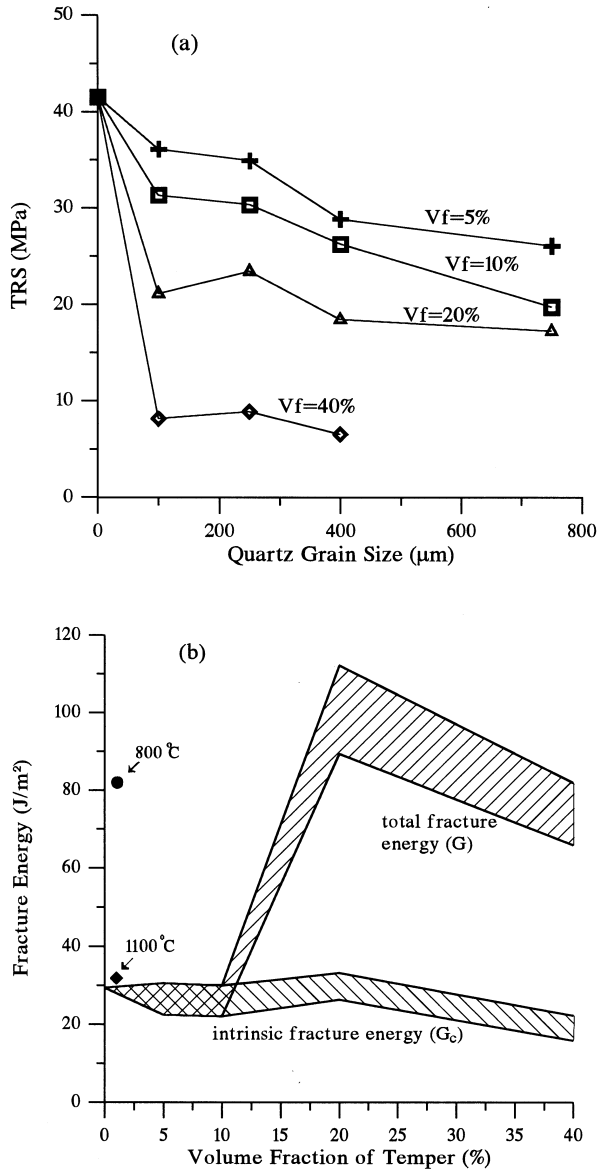
Figure 2   *Results of strength and toughness measurements on quartz-tempered calcareous clay test bars fired at 950°C. (a) Tranverse rupture strength (TRS) as a function of quartz grain size and percentage volume fraction (V$_f$), measured on unnotched bars. Fracture strength (σ$_f$) is approximately equal to TRS/1.5 (Ashby 1992, 18). (b) Fracture energy ranges as a function of percentage volume fraction (V$_f$) of temper, measured on notched bars. Total fracture energy (G) equals intrinsic fracture energy (G$_c$) plus crack propagation energy (G$_t$). The solid black circle and diamond represent the total fracture energy of untempered bars fired at 800°C and 1100°C respectively (after Kilikoglou* et al. *1998, figures 3 and 4).*

about 580°C exerts a tensile stress on the surrounding matrix prior to its vitrification and densification, resulting in microcracking of the previously damaged zone. Finally, during cooling, an equivalent contraction of the quartz occurs and, since the fired clay matrix is unable to follow this contraction, the quartz particles become debonded from the clay matrix. As a result of this debonding, the quartz inclusions act effectively as closed pores, and these pores are the cause of the observed decrease in Young's modulus with increasing quartz content. For a volume fraction of quartz inclusions of about 20% and above, the damaged zones associated with individual quartz particles interact to produce a microcrack network that covers the whole specimen.

Since the intrinsic fracture energy (G_c) depends principally on the strength of the bonding within the vitrified clay matrix, it is essentially unchanged by the addition of quartz temper. The slight decrease observed when the quartz content is increased from 20% to 40% is perhaps due to the resulting poorer packing of the original clay particles and, thus, to some minor change in the microstructure of the vitrified clay matrix formed during subsequent firing. However, the subsequent crack propagation occurs via the microcrack network formed as a result of the addition of quartz temper. Therefore, instead of being approximately straight, the propagating cracks tend to weave from one inclusion to another, resulting in considerable dissipation of energy (G_t) through the crack deflection, bifurcation and arrest. In consequence, the total fracture energy (G), and thus the toughness of the ceramic, increase with increasing concentration of quartz temper. Conversely, the increase in the pore concentration and size, as a result of the formation of microcracks and their interaction to form an overall network, means that the length ($2c$) of the cracks at which crack initiation occurs is increased. As a result of this increase, together with the corresponding reduction in Young's modulus, the fracture strength (σ_f), as determined from equation (1), decreases with increasing concentration of quartz temper. In summary, it is apparent that, for a calcareous clay fired to 950°C, the addition of about 20% quartz inclusions by volume is optimum in that the toughness is maximized without any further unnecessary reduction in the fracture strength.

Kilikoglou *et al*. (1998) also noted that stable fracture, with the associated lower fracture strength but higher total fracture energy, and thus toughness, was observed in untempered test bars when these were fired at low temperatures below about 800°C. Because there is considerably less vitrification of the clay matrix as compared to that for a firing temperature of 950°C, the clay particles are not fully fused together. The intrinsic fracture energy (G_c) is therefore reduced. However, the energy dissipation during crack propagation (G_t) is significantly increased as a result of deflection and bifurcation of cracks at the surviving interfaces between the clay particles, and crack arrest at pores. Therefore, the total fracture energy and toughness are increased at the lower firing temperature. Conversely, the fracture strength is reduced as a result of a combination of increased porosity—that both provides the flaws at which crack initiation occurs and reduces Young's modulus—and a lower intrinsic fracture energy.

Dependence on type of temper

In addition to temper concentration, strength and toughness depend critically on the type of temper added. However, as yet, the role of temper type is less well understood. The experimental data that do exist in the literature suffer from various weaknesses that, in many cases, make them both difficult to compare one with another and difficult to reproduce. The principal reason for this is the lack of adequate information given on the choice and treatment of the raw materials, the preparation of the test pieces and the mechanical testing procedures. In addition, inappropriate testing procedures were sometimes employed. For example, toughness measurements

made on unnotched bars are inherently inaccurate. As a result, the explanations given below for the apparent differences between different sets of experimental data should be regarded as tentative.

In addition to the data published by Kilikoglou *et al.* (1995, 1998), quantitative experimental data on strength and toughness for different types of temper have been presented by Hoard *et al.* (1995), Feathers (1989), Feathers and Scott (1989) and West (1992). Information on the raw materials, preparation of test specimens and measurement procedures used by the different authors are given in Table 1. It must be emphasized that, with the exception of Kilikoglou *et al.* (1995, 1998), who used calcareous clays, non-calcareous clays were chosen as the base material and the test specimens were fired at temperatures well below those required to achieve any significant vitrification. These choices were made because the test specimens were attempting to imitate the fabric of the prehistoric cooking pots from North America (e.g., Late Woodland and Mississippian periods in Missouri) that inspired the studies. In contrast, the choices made in the study by Kilikoglou *et al.* (1995, 1998) were influenced by the high-fired, calcareous pottery most commonly used for transport wares produced in the Aegean and the Mediterranean during the Bronze Age. The published data on fracture strengths (σ_f), intrinsic fracture energy (G_c) and crack propagation energy (G_t) from each of the papers are summarized in Table 2. However, data on the intrinsic fracture and crack propagation energies published in Hoard *et al.* (1995) are not included. This is due, first, to the measurements being made using an unnotched bar, so that there was no control over the dimensions of the flaws at which crack initiation occurred. Second, the intrinsic fracture energy was calculated from the area under the linear rising part of the load–displacement curve and, therefore, included the proportion of the stored energy that had been transformed into kinetic energy. Third, no correction was made for the compliance of the testing machine. As a result of these factors, the values published by Hoard *et al.* (1995) are too high by at least an order of magnitude.

First, considering the observed fracture strengths (σ_f), the data from West (1992) support those from Kilikoglou *et al.* (1995, 1998) in confirming that, as a result of the smaller size and concentration of flaws, the fracture strength for untempered pottery is greater than that for any type of tempered pottery. Furthermore, the fracture strengths observed for quartz temper tend to be less than those for limestone, shell and grog tempers for the same clay matrix and firing temperature (Feathers 1989, West 1992, Hoard *et al.* 1995). This is consistent with the fact that, as discussed above, the quartz temper causes microcracking and becomes debonded from the clay matrix, whereas these effects are less pronounced with limestone, shell and grog temper, because their thermal expansion coefficients are similar to that for the clay matrix.

The significantly higher absolute values for the fracture strengths reported by Kilikoglou *et al.* (1995, 1998) can be explained by a combination of the significantly higher firing temperatures and the properties of the clay employed. Thus, a firing temperature even of 800°C—and certainly one of 950°C—will result in greater vitrification and therefore stronger bonding within the clay matrix than firing temperatures of 600°C and 700°C, as used for the other experimental data sets. Similarly, the fact that the clay used by Kilikoglou *et al.* (1995, 1998) exhibits green strengths (12 MPa for untempered and 6 MPa for tempered bars) greater than the fracture strengths for the fired clay bars reported in the other papers indicates stronger bonding between the original clay particles. As a result, the energy required for crack initiation, and thus the fracture strength, are significantly increased.

Second, considering the observed intrinsic fracture energies (G_c), the values from Kilikoglou *et al.* (1995, 1998) and from West (1992) for untempered specimens are very similar when comparing firing temperatures of 800°C with 700°C and 950°C with 900°C. Furthermore, these

Table 2 *Strength and toughness data*

Firing temperature / Temper type	Transverse rupture strength, TRS* (MPa)					Intrinsic fracture energy, G_c (J m^{-2})			Crack propagation energy, G_t (J m^{-2})		
	1† 800°C (950°C)	*2* 600°C	*3* 600°C	*4* 700°C	*4Q‡* 700°C	*1* 800°C (950°C)	*3A* 600°C	*4* 700°C (900°C)	*1* 800°C (950°C)	*3A* 600°C	*4* 700°C (900°C)
Untempered	25 (42)			4.1	0.6	15 (30)		11 (29)	65 (0)		0.2 (0.2)
Grog		2.6		2.5	0.8			7.6 (14)			0.9 (0.9)
Quartz	(20r)§	2.7g	2.6r	1.7r / 1.8	0.7r / 0.8	(30r)	0.04r	7.3 (14)	(60r)	2.3r	3.9 (7.6)
Limestone		4.2		2.2m	1.0m						
Shell			3.0	2.5	1.3		0.11	12		5.5	5.3
Mica				1.7	1.3			37 (68)			11 (71)
Wollastonite				3.0	2.2			36 (34)			22 (31)

* Fracture strength (σ_f) as used in the text is approximately equal to TRS/1.5 (Ashby 1992, 18).

† Sources: 1, Kilikoglou *et al*. (1995, 1998); 2, Hoard *et al*. (1995); 3, Feathers (1989); 3A, Feathers and Scott (1989); 4, West (1992).

‡ 4Q is TRS measured after specimen quenched from 600°C.

§ Temper: r, rounded temper particles (otherwise angular, platy or fibrous); g, granite temper; m, marble temper.

Original units (where converted) are as follows. Fracture strength: 2, g cm^{-2}; 3, kg m^{-2}; 4, N (breaking load). Fracture/propagation energy: 4, mJ (total energy).

values are within the limits reported in the literature (Ashby and Jones 1996a, 136). However, the West (1992) values were calculated from the area under the linear rising part of the load–displacement curve. Since these values therefore include the proportion of the stored energy transformed into kinetic energy, they could be too high. Lower intrinsic fracture energy values from West (1992), as compared to those from Kilikoglou *et al*. (1995, 1998), might also be expected in view of the much lower fracture strengths reported in West (1992). Furthermore, since the intrinsic fracture energy depends mainly on the strength either of the bonding at the interfaces between clay particles or of the atomic bonding within a vitrified clay matrix, the lower values observed by West (1992) for grog and quartz temper, and the higher values observed for mica and wollastonite temper, are unexpected. It is possible that, as previously suggested to explain the slight decrease observed with increasing concentration of quartz temper (Kilikoglou *et al*. 1995, 1998), these lower values are similarly associated with poorer packing of the clay particles and changes in microstructure resulting from the high concentration of temper. In the case of the higher values, a possible explanation is that these intrinsic fracture energies include a component associated with fracture occurring through platy or fibrous temper particles, rather than the crack being deflected or bifurcated around them.

An additional problem requiring explanation is the very low intrinsic fracture energies (smaller by factors of between 100 and 750) observed by Feathers and Scott (1989) as compared to those observed by either Kilikoglou *et al*. (1995, 1998) or West (1992). Again, because of the much lower fracture strengths observed by Feathers (1989) as compared to those observed by Kilikoglou *et al*. (1995, 1998), lower intrinsic fracture energies might be expected. Also, it is just possible that the lower Feathers and West (1989) values are due to the form of the crack front generated during the chevron-notched-bar (CNB) test as compared to the straight-edge-notched-bar (SENB) test employed by Kilikoglou *et al*. (1995, 1998) and West (1992). However, it is unrealistic to expect that either of these effects could reduce the observed intrinsic fracture energies by factors of between 100 and 750. Therefore, there must be some mistake in the data, one possibility being that the wrong units have been quoted.

Finally, considering the observed crack propagation energies (G_t), the values from Feathers and Scott (1989) and from West (1992) for quartz temper are significantly lower than those for shell temper and, in the latter case, also for mica and wollastonite temper. These high crack propagation energies for platy (shell and mica) and fibrous (wollastonite) tempers, as compared to angular or rounded quartz temper, are due first to the increased dissipation of energy associated with the deflection and bifurcation of the crack at the interfaces between such elongated inclusions and the clay matrix. Second, such inclusions are more effective at bridging propagating cracks so that additional energy must be expended either in fracturing the inclusions or in overcoming the friction associated with pulling them out from the clay matrix.

The absolute values for the crack propagation energies for quartz temper and for shell temper that were observed by Feathers and Scott (1989) and West (1992) for firing temperatures of 600°C and 700°C, respectively, are similar. Furthermore, the values from West (1992) for quartz-, mica- and wollastonite-tempered specimens fired at 900°C are higher than those for specimens fired at 700°C. However, in the case of the quartz-tempered specimen, the value from West (1992) is still lower than that from Kilikoglou *et al*. (1995, 1998) for their quartz-tempered specimen fired at 950°C. These latter observations probably reflect changes in the energy dissipated in crack deflection and bifurcation, resulting from both differences in the original packing of the clay particles, and increasing vitrification and thus strength of bonding within the clay matrix with increasing firing temperature.

Furthermore, as previously observed by Kilikoglou *et al*. (1995, 1998), the data from West

(1992) also indicates that the crack propagation energy for untempered pottery fired at 900°C is significantly less than that for tempered pottery (except grog-tempered) fired at the same temperature. However, in contradiction to the observation by Kilikoglou *et al.* (1995, 1998) for untempered pottery fired at 800°C, West (1992) again observed a low value for the crack propagation energy for untempered pottery fired only to 700°C. A possible explanation is that the rate of loading of the specimens during the West (1992) bending tests was too rapid so that, as in the case of the impact method of measurement, there was insufficient time for the system to absorb the energy offered to it. As a result, the intrinsic fracture energy values tend to be too high and the crack propagation energy values tend to be correspondingly too low.

In summary, it is apparent that, as observed previously for quartz temper, the addition of temper to clay results in a reduction in the fracture strength but an increase in the toughness of the resulting pottery. Furthermore, it appears that platy or fibrous tempers, as compared to angular or rounded quartz temper, maximize the increase in toughness while tending to minimize the reduction in the fracture strength. However, it is also clearly apparent from the above discussion that our current understanding of the role of different types of temper in determining the fracture strength and toughness of pottery is far from being complete, and further more comprehensive and more carefully controlled measurements are required.

THERMAL SHOCK RESISTANCE

The thermal shock resistance of pottery vessels provides a measure of their ability to survive rapid changes in temperature without fracture. As with strength and toughness, in order to understand and assess thermal shock resistance one needs to consider, first, the initiation of cracks and, second, the propagation of these cracks to the ultimate failure of the vessel (Hasselman 1963, 1969; Kingery *et al.* 1976, 816).

The primary driving force for crack initiation in thermal shock is the stresses due to the differential expansion or contraction of the inner and outer surfaces of a pottery vessel resulting from a rapid change in temperature at one surface, and thus temperature gradients through the vessel wall. Assuming that there is insufficient time for heat conduction between the two surfaces, the stress (σ) that results from a temperature difference (ΔT) is given by

$$\sigma = SE\alpha\Delta T/(1 - \mu),$$

where E is Young's modulus, α is the linear thermal expansion coefficient, μ is the Poisson ratio and S is a geometrical constant determined by the shape of the vessel. Hence, crack initiation occurs when the temperature difference (ΔT_c) between the two surfaces is sufficiently high that the resulting stress is equal to the fracture strength (σ_f) of the ceramic; that is,

$$\Delta T_c = \sigma_f(1 - \mu)/SE\alpha. \tag{2}$$

A possible secondary driving force is the stresses that occur during heating, when the thermal expansion of the temper particles is greater than that of the clay matrix. This is a potential problem with quartz temper because of the expansion associated with the α–β phase transition at about 580°C. However, these stresses are less severe than sometimes suggested, because the greater shrinkage of the quartz particles, as compared to the clay matrix, during cooling subsequent to the original firing will have resulted in debonding between the quartz temper and the clay matrix. This debonding is clearly visible in SEM photomicrographs, and the resulting spaces around the quartz temper are the reason for the decreasing values for Young's modulus with increasing concentration of quartz temper (Kilikoglou *et al.* 1995, 1998). Therefore, during
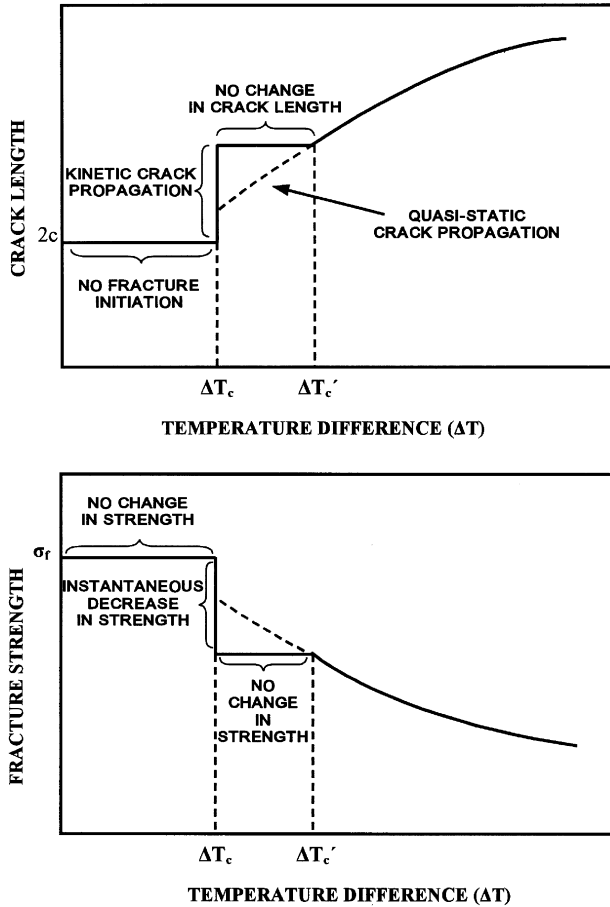
Figure 3 *Variation in crack length in and fracture strength of a ceramic as a function of increasing the temperature difference (ΔT) between its two surfaces by rapidly changing the temperature at one surface. 2c and σ_f are the original crack length and fracture strength respectively (after Hasselman 1969, figure 2).*

subsequent heating, the temper particles can expand into these spaces. Even so, since the observed thermal expansion of quartz tempered pottery clearly includes a component associated with the $\alpha-\beta$ phase transition, the spaces due to debonding only partially accommodate the quartz expansion and some stresses will therefore still be generated. However, these stresses are lower when the porosity created by loose packing of the clay particles is high, since there is then more space to accommodate expansion.

Since fracture by thermal shock generally takes place without any applied external load, the driving force for crack propagation is provided by the elastic energy stored in the body at the moment when the temperature difference (ΔT_c) is sufficient for the onset of crack initiation. In order to understand the subsequent crack propagation, Hasselman (1969) followed the Griffith approach and considered the energy balance between the stored elastic energy and the surface energy of the crack. He was thus able to show that the variation in the critical temperature difference (T_c) with increasing crack length goes through a minimum, with the region of crack stability bounded by two values of crack length. This behaviour contrasts with that for

constant external load, in which fracture strength decreases progressively with increasing crack length.

For short initiating cracks, the decrease in stored elastic energy with increasing crack length exceeds the corresponding increase in surface energy. Therefore, as with a constant external load, the excess energy is transformed into kinetic energy of the moving crack. However, in this case, crack propagation only continues until all the stored elastic energy associated with the temperature difference (ΔT_c) is dissipated. Once the crack has been arrested, further elastic energy—and thus a further increase in the temperature difference driving fracture, to a new value ($\Delta T_c^{'}$)—are necessary in order for crack propagation, which is now quasi-static, to continue. The increase in crack length and corresponding decrease in fracture strength as functions of the stored elastic energy measured in terms of the temperature difference between the two surfaces of the ceramic are illustrated in Figure 3. Hasselman (1969) further showed, again for short initiating cracks, that the final crack area at the point at which the crack is arrested is inversely proportional to the original crack length ($2c$). Therefore, from equation (1), the final crack area is proportional to σ_f^2/GE, where σ_f is the fracture strength at crack initiation and G is the total fracture energy, again equal to ($G_c + G_t$).

On the basis of the above theory, it is apparent that there are two approaches to designing and selecting materials for high thermal shock resistance. The first involves the avoidance of crack initiation and for this, the temperature difference (ΔT_c) necessary for the onset of crack initiation must be maximized. Assuming that the rate of change of temperature is such as to allow time for heat conduction between the two surfaces, then, on the basis of equation (2), the appropriate thermal shock resistance parameter (R_{ci}) is given by

$$R_{ci} = K\sigma_f(1 - \mu)/E\alpha,$$

where K is the thermal conductivity. The second approach involves the avoidance of catastrophic crack propagation and, for this, the area over which the cracks propagate before being arrested must be minimized. In this case, the appropriate thermal shock resistance parameter (R_{cp}) is given by

$$R_{cp} = GE/\sigma_f^2(1 - \mu) = (G_c + G_t)E/\sigma_f^2(1 - \mu).$$

Thus, maximization of the thermal shock resistance by avoidance of crack initiation (i.e., high R_{ci}) requires materials with high fracture strength and thermal conductivity, and low Young's modulus and thermal expansion. Conversely, maximization of the thermal shock resistance by minimizing crack propagation (i.e., high R_{cp}) requires materials with high total fracture energy and Young's modulus, and low fracture strength.

On the basis of the results presented in the previous section, the high fracture strength necessary for high R_{ci} requires a ceramic with low temper concentration and high firing temperature. However, crack initiation as a result of thermal shock can still occur fairly readily in such a ceramic—and when it does occur, propagation is excessive and catastrophic failure is the likely consequence. In contrast, the high total fracture energy or toughness necessary for high R_{cp} requires a ceramic with high temper concentration and, normally, a low firing temperature. In this case, the propagating crack will be stopped more rapidly as a result of energy dissipation through crack deflection and bifurcation at the temper/clay matrix interfaces, and crack arrest at pores (G_t). In these circumstances, although weakened, the ceramic will survive and can continue to be used. As also discussed above, this increase is maximized by the use of platy or fibrous temper particles, since additional energy is dissipated during crack propagation either in fracture of such particles or in pulling them out from the clay matrix.

In this context, it should be emphasized that the behaviour of thermal cracks during initial propagation is similar to that of cracks resulting from impact. Again, there is the possibility of insufficient time to absorb the associated stored elastic energy so that energy dissipation during crack propagation is less than expected. Conversely, by opening up under additional stress, a network of microcracks can reduce the stress concentrations associated with thermal shock. Thus, the thermal shock resistance of a previously mildly shocked ceramic can be increased substantially.

The temper added to a ceramic can also influence the thermal shock resistance associated with the avoidance of crack initiation (R_{ci}) through its contribution to the bulk thermal expansion. Thus, tempers such as limestone and shell with comparatively low thermal expansion coefficients result in a higher R_{ci} than quartz temper with its high expansion coefficient in the temperature range up about 580°C. These tempers, as well as grog, also result in a higher R_{ci} than quartz temper because their thermal expansion coefficients are similar to that of the clay matrix and there is, therefore, no differential thermal expansion to generate stresses during heating.

Measurements of thermal shock resistance

As in the measurement of fracture strength, in measuring thermal shock resistance it is important to distinguish between the values applicable to an entire vessel and those measured on test pieces made from the same material. For example, since the magnitude of the stresses generated by thermal shock is dependent on vessel shape, globular-shaped bodies have higher thermal shock resistance than those with a sharp angle at the junction between base and wall. Similarly, the wall thickness and vessel contents can affect thermal shock behaviour as a result of differences in temperature gradient and thermal capacity, respectively.

Thermal shock resistance is normally measured in terms of the strength degradation in test bars observed following their subjection to a series of rapid temperature changes. More recently, Daszkiewicz *et al.* (2000) have suggested that changes in either the propagation velocity of longitudinal ultrasonic waves or the water permeability across a sherd or test bar before and after thermal shock could be used as a measure of thermal shock resistance. A reduction in the velocity of ultrasonic waves indicates that the microcrack density has increased as a result of thermal shock, whereas an increase in the water permeability indicates the formation of macrocracks. The first method is sensitive to very slight increases in microcrack density that are insufficient to cause significant deterioration of a pottery vessel. Therefore, the authors suggest that the water permeability method provides a more useful measure of thermal shock resistance.

The most comprehensive data on the role of different types of temper in achieving high thermal shock resistance are those reported by West (1992), who used three-point bending to measure strength degradation. Measurements were made on test bars, tempered with a wide range of materials, both before and after they had been subjected to quenching from progressively higher temperatures up to 600°C (TRS columns 4 and 4Q in Table 2). These results established that the test bars for which the loss of strength was least were those tempered by platy or fibrous inclusions, such as mica (23% loss of strength after quenching from 600°C), wollastonite (26% loss) and shell (45% loss). The strength losses were greater for test bars tempered with marble (55% loss), quartz (58% loss) and sand (59% loss) which were either angular and rounded, and were greatest for grog-tempered (69% loss) and untempered (86% loss) test bars.

The high strength loss after quenching for grog temper is perhaps surprising, since the thermal expansion of grog is very similar to that of the clay matrix. However, because of this similarity in

thermal expansion coefficients, the grog temper remains in close contact with the clay matrix and, at the same time, the mechanical properties of the grog and clay matrix are also similar. Therefore, cracks tend to pass through the grog temper rather than being deflected and bifurcated, as in the case of quartz and sand temper. As a result, the dissipation of energy occurring during crack propagation is less, and this reduction is not compensated for by the reduced stresses that result from the similar thermal expansion coefficients of the grog and matrix.

Bronitsky and Hamer (1986) and Skibo *et al.* (1989) have also undertaken strength degradation measurements on test bars using impact testing with pendulum and falling weight systems, respectively. The energies required for shattering were measured for test bars before and after they had been subjected to some 40 cycles of quenching from boiling water into iced water. Apart from again confirming that the loss of strength was greatest for untempered test bars, these results were both less comprehensive—in that only quartz sand, shell or organic (grass and manure) temper was used—and less conclusive.

MECHANICAL AND THERMAL PROPERTIES OF ARCHAEOLOGICAL AND ETHNOGRAPHIC CERAMICS

Having summarized the available data on the role of clay, temper and firing temperature in determining the strength, toughness and thermal shock resistance of clay ceramics, it is now necessary to review a selection of the work that has been published relating to the mechanical and thermal properties of archaeological and ethnographic pottery. In particular, we want to assess to what extent the choice of clay, temper and firing temperatures might have been influenced by a desire to achieve specific mechanical and thermal properties that were beneficial in use. The diverse geographical (North America, Europe, Near East) and chronological (Neolithic to present day) range of the work reviewed reflects the limited extent and uneven pattern of mechanical and thermal property studies of archaeological and ethnographic ceramics.

Before attempting such an assessment, it is important to emphasize that the production technology represents just the initial stage in the complete life-cycle of pottery, the subsequent stages being distribution, use, reuse and discard. This life-cycle is itself firmly embedded in the overall environmental, technological, economic, social, political and ideological contexts. The myriad different technological choices (i.e., clay, temper, forming, surface treatment, firing, and so on) that are possible in pottery production are in turn determined, in a highly complex fashion, by these contexts (Kilikoglou *et al.* 1998, 275; Sillar and Tite 2000). At a practical level, there is the availability and the performance characteristics of the raw materials, tools, energy sources and techniques used in the production of the pottery. However, of equal importance is the potters' perception of the technological choices made, as well as the consumers' perception of these choices and/or the resulting finished product. These technological choices define the 'technological style' that, as proposed by Lechtman (1977) and developed by Lemonnier (1986), resides in every stage of a production process and that, like morphological and decorative styles, can serve as an expression of social or cultural identity. An example is the use of grog temper. In a number of ethnographic contexts, this reuse of old pottery as temper in new pottery is seen as an act of 'rebirth', in which a 'reversal of time' is achieved (Barley 1994).

In the context of archaeological ceramics, probably the most studied functional requirement for any pottery vessel has been the high thermal shock resistance required by cooking pots in order that they could survive the repeated rapid changes in temperature to which they were inevitably subjected in use. In contrast, strength and toughness, although intimately related to

thermal shock resistance, have been much less studied. In part, this is because, although the ability to retain their contents was an essential performance characteristic for all types of pottery vessel, the strength requirements to achieve this were normally not too demanding. Conversely, although the toughness requirements to survive impact were again potentially demanding, impacts are in most cases accidental and, therefore, it has been assumed that the risk of damage to vessels from impact was minimized by care in their use.

Strength and toughness

Neupert (1994) has undertaken strength measurements on Cibola White Ware from the southwestern United States, using a ball-on-three-ball tester. The results showed that, over the period from AD 700 to AD 1200, there was a progressive change in the temper used from predominantly smooth-surfaced sand temper to predominantly rough-surfaced grog temper and that, as a result, the strength of the Cibola White Ware was increased by about 70%. However, Neupert was unable to identify any specific functional reasons why the Cibola potters might have wanted to increase the strength of their pottery. Instead, he had to resort to the general statement that the increased strength served 'to extend vessel use life, broaden vessel function, and facilitate the expansion of trade and exchange networks'. In these circumstances, one must ask whether, rather than aiming to increase strength, there was some completely different reason for the change in the type of temper used by the Cibola potters.

The principal vessel types for which strength and toughness were potentially important properties were large vessels used as containers during transportation and for storage. Any increase in strength necessary to ensure that such vessels were able to retain their contents could normally have been achieved fairly easily by increasing the thickness of the vessel wall. However, achieving the toughness required for vessels used as containers during transportation, so that they were able to withstand accidental impacts during stacking or as a result of movement in transit, could have been more difficult. Vekinis and Kilikoglou (1998), using data from Hertzian strength and wear resistance measurements, have estimated the strength and toughness of fifth-century BC Punic amphorae found at Corinth and probably produced in northern Morocco. Their results show that the two groups of amphorae, previously identified by Maniatis *et al.* (1984) on the basis of their chemical compositions, petrography, vitrification and porosity, have different strengths and toughnesses. The higher values are associated with the group of amphorae that were made from clays with higher calcium oxide contents and smaller inclusion sizes, and that have higher porosity. However, Vekinis and Kilikoglou were again unable to suggest any convincing reason as to why this particular group of amphorae might have benefited from the increased strength and toughness thus achieved. Therefore, one must ask whether there were some alternative reasons for the change in clay type and porosity for this group of amphorae.

Kilikoglou and Vekinis (1998) have also recently started to investigate the potential of finite element analysis for predicting failure in archaeological pottery. This approach, which only requires knowledge of Young's modulus (either measured or inferred from microstructure and/ or composition) and the vessel's dimensions, involves first dividing the vessel into a large number of virtual elements. The strain experienced by every part of the vessel is then calculated under various loading modes (e.g., freely supported by the handles, free-standing, supported by the circumference, and so on) for a range of applied loads. For each loading mode, it is possible to identify the point at which the strain is maximum and at which failure is therefore most likely to occur. By comparing these results with known failure strains for the material in question, the

load at which failure will occur can then be predicted. In this way, it should be possible to investigate the suitability of a particular vessel shape for the loading modes associated with different possible uses of the vessel and thus, perhaps, provide an explanation for observed changes in shape of, for example, transport amphorae.

Thermal shock resistance

Braun (1983) attempted to explain the observed changes in technological choice in the production of cooking vessels in terms of a need for different performance characteristics. He showed that, in Illinois and Missouri during the Woodland period, there was a reduction in wall thickness of the pottery and a decrease in concentration and average size of the quartz sand and crushed rock temper around AD 400–500. He argued that these changes reflected the increasingly stressful thermal conditions to which pottery was subjected as a result of the longer cooking times associated with the increasing importance of starchy seed foods. Thus, the observed reduction in wall thickness resulted in more rapid conduction of heat from the exterior to the interior and, hence, in an improved heating effectiveness. At the same time, the temperature gradients through the vessel wall and, therefore, the stresses driving crack initiation during thermal shock, are reduced. On the debit side, the reduction in wall thickness resulted in a decrease in strength. However, this was compensated for by the increase in strength achieved through a decrease in the concentration and average size of the temper. This decrease in the amount of temper could have resulted in a decrease in the dissipation of energy during crack propagation and, therefore, a decrease in thermal shock resistance. However, as shown by Kilikoglou *et al.* (1998), provided that the amount of temper does not fall below about 20% by volume, the contribution to the total fracture energy from crack propagation remains essentially constant with decreasing temper content. In addition, the reduction in the amount of high thermal expansion quartz-rich temper also resulted in a decrease in the bulk thermal expansion and, thus, a decrease in the stresses driving crack initiation during thermal shock.

Subsequently, Steponaitis (1983, 1984) showed that, in the region around Moundville, Alabama, during the period from 1000 BC to AD 1500, the temper type used in cooking pots changed sequentially from plant fibre to coarse quartz sand, then to fine quartz sand, to grog and, finally, to coarse shell during the Mississipian period. He argued, therefore, that coarsely ground shell provides the most appropriate temper for cooking pots and that the use of shell temper can be seen as the final stage in a technological development aimed at achieving the 'ideal' cooking pot. The first advantage of shell temper was that, as discussed above, the platy shell particles were more effective at stopping crack propagation than rounded or angular quartz sand or grog particles and, thus, resulted in a higher thermal shock resistance. The second advantage was that, because the thermal expansion of shell temper was significantly lower than that of quartz, the bulk thermal expansion with a shell-tempered body was lower than that of a quartz-tempered body and, therefore, the stresses driving crack initiation during thermal shock were less. Finally, any stresses that occurred during heating, as a result of the greater thermal expansion of the quartz temper as compared to the clay matrix, were absent in the case of shell temper.

More recently, Hoard *et al.* (1995) have highlighted the extensive use of limestone temper in cooking pots from many areas of North America. They argue that, although crushed limestone, being angular in shape, is not as effective in stopping crack propagation as the platy shell particles, the thermal expansion coefficient of limestone is the same as that for shell. Therefore, the bulk thermal expansion of a limestone-tempered body is lower than that of a quartz-tempered body, thus again reducing the stresses driving crack initiation during thermal shock.

Furthermore, they argue that, because the calcium ions released from the limestone improve the working properties of a soft, sticky clay, its addition as temper allows the vessels to be made with thinner walls and to be more globular in shape, both of which result in an increase in thermal shock resistance.

Contrary to the above studies, Woods (1986) questioned the emphasis put on the thermal shock resistance of cooking pots and, in particular, on the importance of shell temper. She showed that, in Britain from the Neolithic through to the medieval period, there is little evidence for the deliberate use of a specific temper type in cooking pots, and that quartz sand was probably more commonly used than shell temper. Therefore, she argued that the crucial characteristic of cooking pots was that they were coarse-textured and that, if they survived the rapid heating and cooling associated with the open firing during their production, they would survive use for cooking. Strictly, the latter argument is not entirely valid, since it takes no account of the cumulative effect of the repeated heating and cooling resulting from use in cooking. Even so, evidence from around the world confirms that a very wide range of temper types was, and is continuing to be, successfully used in the production of cooking pots.

A further group of cooking pots whose resistance to thermal shock has been assessed is the so-called 'brittle ware' pottery produced in the Near East from the Hellenistic through to the early Islamic period (Bartl *et al*. 1995). Brittle ware again contains high concentrations of temper, fine-grained quartz predominating. Daszkiewicz *et al*. (2000) have undertaken a detailed study of Roman brittle ware from Palmyra in Syria, including an assessment of thermal shock resistance on the basis of water permeability measurements before and after tenfold quenching from 400°C into water. Prior to the permeability measurements, the sherds were boiled in distilled water and refired at 400°C in air in order to try to remove any contamination from the pores either resulting from use in antiquity or occurring during burial. This study established, first, that the brittle ware two-handled pots and casseroles, that had clearly been used for cooking, survived repeated quenching without any significant change in permeability. In contrast, the permeability of the majority of the brittle ware jugs and bowls had increased significantly after quenching. Firing temperature estimates, based on the refiring temperature at which changes in as-received values for open porosity, apparent density and water absorption were observed, suggest that the two-handled pots and casseroles were fired in the ranges 900–1000°C and 1000–1050°C, respectively, and the jugs and bowls in the range 800–900°C.

Considering next the type of clay used for making cooking pots, one might expect non-calcareous clays to be favoured, because of their lower thermal expansion coefficient as compared to calcareous clays (Paynter and Tite 2001). Thus, during the Bronze Age in the Aegean, it appears that non-calcareous clays, tempered variously with limestone, schist, phyllites and basalt, were deliberately selected for cooking pots, even when calcareous clays were used for the majority of the other pottery types (Day *et al*. 1997). Similarly, the brittle ware cooking pots from the Near East, referred to above, were made from non-calcareous clays (Bartl *et al*. 1995). Conversely, during the Bronze Age in the Near East, calcareous clays, tempered variously with limestone, shell and basalt, were frequently used in the production of cooking pots (Daszkiewicz and Schneider 1996). Again, in an ethnoarchaeological study of traditional pottery production in Portugal, Picon (1995) showed that both non-calcareous and calcareous clays were used in the production of cooking pots. In this case, the non-calcareous clays were sometimes fired at temperatures up to 900°C, whereas the calcareous clays were always fired at temperatures below 750°C.

Finally, it should be emphasized that there is both historical and ethnographic evidence that consumers were aware of the thermal properties associated with different types of pottery, and

that these properties were a factor in determining their choice as between the available products. Thus, Adan-Bayewitz (1993, 39), in a study of Roman Galilean pottery, noted that second-century AD Rabbinic sources state that water-filled pottery vessels used to make a barrier to prevent the spread of fire must come from specific production centres; otherwise, they will crack and extinguish the fire. He further showed that one of these production centres, Kefar Hananya, specialized in the production of cooking pots during both the Roman and early Byzantine periods. Similarly, in an ethnoarchaeological study of pottery use among the Kalinga of the Philippines, in which consumers were questioned about their reasons for purchasing specific cooking pots, Aronson *et al.* (1994) found that pots produced by one group of potters were favoured. This was because they were perceived to be stronger and hence more durable. Subsequent laboratory tests on the pottery suggested that this perception was essentially correct. Again in an ethnoarchaeological study, Carlton (private communication) has observed in the West Balkans that cooking pots tempered with limestone survive, and are generally known to survive in use, without obvious deterioration, for longer periods than those tempered with quartz sand.

CONCLUSIONS AND FURTHER WORK

On the basis of the theoretical considerations and the experimental data presented above, it is clear that, in general terms, to produce pottery with high strength requires a low temper concentration and a high firing temperature. Conversely, to produce pottery with high toughness and high thermal shock resistance requires a high temper concentration and a low firing temperature.

However, as is apparent from our critical survey of published experimental data, the current understanding of the factors determining the strength, toughness and thermal shock resistance of clay ceramics is still far from complete. Therefore, for the future, the systematic strength and toughness measurements, undertaken on quartz-tempered pottery test pieces by Kilikoglou *et al.* (1995, 1998), should be extended to include other temper types—in particular, shell, limestone and grog—used in the production of archaeological pottery. In addition, the firing temperatures used to produce the test pieces should be extended to cover the range 600–1000°C. Also, because of the different thermal expansion of non-calcareous and calcareous clays, the different tempers should be added to both types of clay, and the thermal expansion coefficients of at least a selection of these test pieces should be measured in the temperature range up to 500°C. Finally, to supplement these data and to provide a more direct measure of thermal shock resistance, measurements of the degradation of the strength of test pieces subjected to a series of rapid temperature changes, as previously undertaken by West (1992), should be extended. Thus, strength degradation measurements should be undertaken on test pieces made from non-calcareous and calcareous clays, either untempered or tempered with quartz, shell, limestone or grog, and fired to temperatures in the range 600–1000°C. In addition, the application of finite element analysis, proposed by Kilikoglou and Vekinis (1998), could usefully be extended to vessels with a ranges of shapes and predicted uses.

As yet, there is no convincing evidence that strength and toughness requirements have been a significant factor in influencing technological choice, even for large vessels used as containers in transportation and for storage. Conversely, in spite of the wide range of tempers and clays used for cooking pots, the overall evidence suggests that the requirements for thermal shock resistance have played an important role in the technological choices made in the production of cooking vessels. Thus, in order to maximize the energy dissipation during crack propagation

and thus minimize the risk of catastrophic crack propagation (i.e., to maximize the thermal shock resistance parameter R_{cp}), cooking pots routinely contain high concentrations of temper and are normally fired at comparatively low temperatures.

One consequence of these high temper concentrations and low firing temperatures is the associated high porosity and permeability of the vessel wall, and hence the reduced heating effectiveness of the resulting cooking pot. This problem can be overcome by the application of an impermeable coating to the interior surface of the pot (Schiffer 1990). However, Schiffer *et al.* (1994) have shown that this coating can result in an increase in the temperature gradient across the vessel wall and hence a reduction in thermal shock resistance. Therefore, in terms of a specific performance characteristic, the actual technological choices made can frequently represent a compromise.

The extent to which shell or limestone temper was deliberately chosen specifically because of either the resulting reduced bulk thermal expansion of the body or, in the former case, its increased effectiveness in stopping crack propagation is less clear. However, because of the risk of spalling (i.e., lime blowing) and the consequent development of a number of ways to overcome the problem, it seems probable that, when shell or limestone was used as temper, the choice was deliberate. One solution to the problem of spalling has been to exercise care in firing so that the temperature does not reach much above about 650°C in an oxidizing atmosphere, or much above about 750°C in a reducing atmosphere, thus preventing decomposition of the calcite. An alternative approach has been to wet the clay with sea water or to add a few per cent of sodium chloride to the clay, thus inhibiting the decomposition of the calcite (Rye 1981). Finally, spalling has been reduced or even eliminated by quenching the vessel, immediately after firing and while still red-hot, in cold water (Laird and Worcester 1956). Since shell- and limestone-tempered pots are equally difficult to fire, it seems probable that lower bulk thermal expansion and/or improved working properties, common to both, were more important than the increased effectiveness in stopping crack propagation associated only with platy shell temper.

In order to extend our understanding of the role of thermal shock resistance in influencing technological choice in the production of cooking pots, it would be valuable to build up a systematic database of information on the clays, tempers and firing temperatures used in the production of cooking vessels from a fully comprehensive, world-wide range of archaeological and ethnographic contexts. At the same time, the clays, tempers and firing temperatures used to make cooking pots should be compared with those used in the production of other types of pottery vessel.

Overall, however, it is obvious that, even on the basis of current evidence, there are many alternative clays, tempers and firing temperatures that can be used in production such that the resulting pottery still adequately satisfies the strength, toughness and thermal shock requirements in use. Thus, it is generally inappropriate to view ancient potters as struggling to cope with the various negative effects of their environment and, thus, needing to undertake a series of systematic experiments to establish the technological choices appropriate to achieving the performance characteristics required in use. The statement by van der Leeuw (1993) that 'The non-availability of the appropriate raw material(s) turns out to be only very rarely the limiting constraint in the manufacture of pottery' provides therefore an appropriate framework within which to consider technological choice.

Conversely, however, as previously argued by Kilikoglou *et al.* (1998, 276), an understanding of the constraints imposed by the strength, toughness and especially thermal shock resistance requirements for pottery provides a valuable baseline for the consideration of the overall reasons for the technological choices associated with their production. Thus, a knowledge of the extent

to which, for example, the thermal shock resistance of cooking pots has been optimized is clearly extremely helpful when trying to establish how the myriad other factors might have affected the technological choices made in the production pots.

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