

it is desired to model seems debatable. There may simply not be a single canonical structure appropriate to vitreous packings generated in unspecified experimental conditions. In any case it seems necessary to assert that, in view of the above results, the Bernal-Cohen-Turnbull view of the random close-packed structure as one essentially determined by hard-sphere repulsions and a particular, limited set of basic polyhedral relationships may need refinement when applied to the aggregation of real atoms under definite thermodynamic and mechanical constraints.

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Examination of ancient pottery using the scanning electron microscope

A SEQUENCE of pottery sherds from Iraq spanning the period about 6000 BC to 750 AD and two sherds from Turkey about 5000 BC have been examined using a scanning electron microscope (SEM). This examination provided information on the internal morphology developed during firing and in particular information on the extent of vitrification (the glassy phase) and the pore structure^{1,2}. The extent of vitrification provided a useful parameter for characterising the quality of the pottery since it influences several physical properties (such as, hardness, strength, permeability) which are relevant to its suitability for the various uses to which it might be put. In addition by refiring samples of the pottery at known temperatures and determining, by re-examination with the SEM, the temperature at which an increase in the vitrification had occurred, it was possible to estimate the firing temperature used in antiquity.

Fresh fracture surfaces in the pottery, coated with a thin layer of Au–Pd, were examined in a SEM (Cambridge S600) both before and after refiring at known temperatures in the range 750 to 1,250 °C. The refirings were carried out in a tubular furnace in air at a heating rate of 200 °C h⁻¹ with a soaking time of 1 h at the peak temperature.

The nature of the internal morphology observed with the SEM together with X-ray powder diffraction data established that all the pottery was manufactured from calcareous clays. On the basis of the stage which had been reached in the progressive development of vitrification, it was possible to divide the pottery into four groups (Table 1). The first group (NV) contains pottery in which there is no vitrification and the

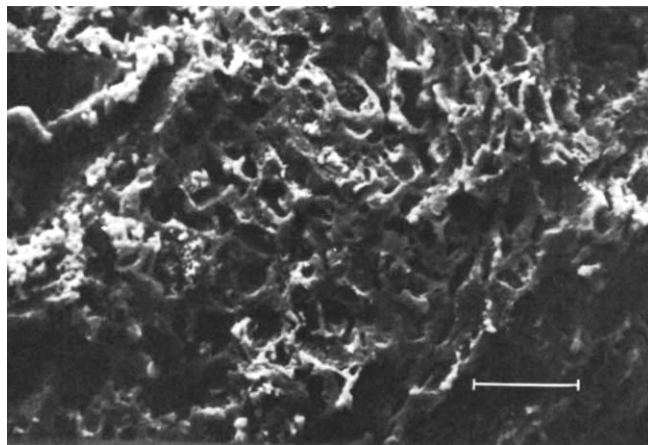


Fig. 1 Scanning electron micrograph of extensively vitrified pottery sherd (V) from Nineveh (Neo-Assyrian), Iraq. Bar represents 10 μm.

aggregates of flaky clay particles are essentially the same as in raw clay. The second group (V) exhibits extensive vitrification with a network of smooth-surfaced glass filaments forming an open or cellular structure over the fracture surface (Fig. 1). In the third group (V+), the cellular structure has begun to coarsen and larger areas of glass are present. Finally the fourth group (TV) exhibits total vitrification, the cellular structure having disappeared and been replaced by a continuous vitrified surface containing isolated pores (Fig. 2).

By means of refiring experiments on the pottery, together with the data obtained from examining specimens of calcareous clays fired at known temperatures and showing a similar pattern of vitrification development, it was possible to assign approximate firing temperature ranges to the various vitrification stages as indicated in Table 1. In assigning these ranges, it was assumed that the firing times (heating plus soaking time) employed in manufacture were comparable with those employed during refiring. Significantly faster heating rates (say 800 °C h⁻¹) and shorter soaking times (5 min) would have required firing temperatures higher by about 50 °C to achieve the same extent of vitrification. Second, on the basis of the colour of the pottery, it was assumed that it had been fired in an oxidising atmosphere. If fired in a reducing atmosphere, firing temperatures lower by about 50 °C would have produced an equivalent vitrification.

The pottery from Iraq was all fired to sufficiently high temperatures to produce, at least, extensive vitrification (V)

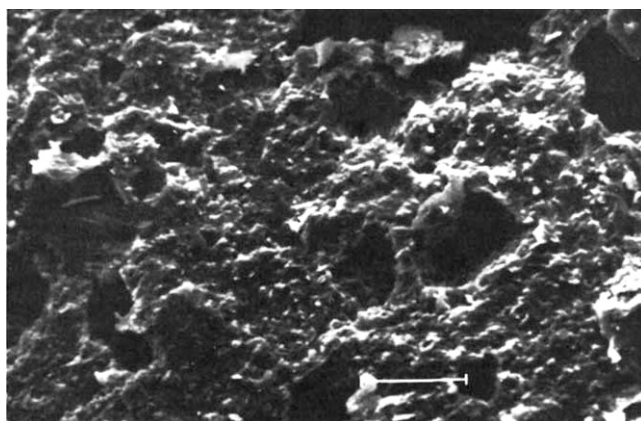


Fig. 2 Scanning electron micrograph of totally vitrified pottery sherd (TV) from Ubaid, Iraq. Bar represents 10 μm.

Table 1 Vitrification stage and firing temperature of ancient pottery

Provenance*: Period	Approximate time ranges	Number of sherds			
		NV < 800 °C	V 850–1050 °C	V+ 1050–1150 °C	TV > 1150 °C
Choga Mami (Jarmo)	c. 6000 BC		1		
Samarra	c. 5500–5000 BC		2	1	
Arpachiyah (Halaf)	c. 5000–4500 BC		4		
Ubaid, Ur, Eridu (Ubaid)	c. 4500–4000 BC		1	2	4
Nineveh: IV/V	c. 3500–2800 BC		3	1	1
Jemdet Nasr	c. 3500–3000 BC		1	1	
Kish: Early Dynastic	c. 2900–2400 BC		3		
Kish: Old Babylonian	c. 1800 BC		1		
Nineveh: Neo-Assyrian	c. 800–600 BC		2		
Nineveh, Kish: Parthian	c. 150 BC–250 AD		3		
Kish: Sasanian	c. 250–650 AD		1		
Hacilar	c. 5000 BC	2			

*Type-site given in brackets where this differs from provenance. Except for Hacilar, which is in Turkey, all the sites are in Iraq.

and for most of the periods under consideration, this group predominates (Table 1). The principal exception is the Ubaid pottery which exhibits chiefly total vitrification (V+ and TV), indicating that consistently higher firing temperatures were employed during this period. It is therefore apparent that the technology required to manufacture extensively vitrified pottery using calcareous clays was developed in Iraq at a very early stage in the production of pottery and that this tradition in ceramic technology remained essentially unchanged over a 6,000-yr period. Furthermore the tradition in Iraq contrasts with that in Turkey during the period around 5000 BC where, although calcareous clays were again used, the firing temperatures employed were significantly lower and the pottery produced exhibits no vitrification (NV).

The use of calcareous clays, although obviously determined in part by their availability, is of interest since this type of clay possesses distinctive vitrification properties which facilitate firing². First, extensive vitrification (V) can be achieved at the comparatively low firing temperature of about 850 °C. Second, the characteristic cellular structure associated with extensive vitrification remains essentially unchanged over a temperature range of about 200 °C (from 850 to 1,050 °C) and therefore the control of the temperature attained during firing is not particularly critical. This contrasts with the situation for non-calcareous clays where the extent of vitrification increases progressively with increasing temperature so that the quality of the pottery produced can vary quite considerably with changes in firing temperature of about 50 °C. But in the context of estimating the firing temperatures employed in antiquity, the thermally stable structure associated with calcareous clays results in a wide temperature range being assigned to the extensive vitrification group (V) in Table 1.

These results establish that, because information is obtained on both the extent of vitrification and the firing temperature, the examination of ancient pottery with an SEM is valuable for characterising and distinguishing between the different traditions in ceramic technology in antiquity. Since the firing temperature required to produce a particular degree of vitrification can vary by as much as 200 °C, depending on the refractoriness of the clay and the firing atmosphere used, either the extent of vitrification or the firing temperature by itself does not fully characterise the ceramic technology. For example, the same extent of vitrification can be achieved by firing a calcareous clay at a low temperature (850 °C) or a refractory non-calcareous clay at a higher temperature (950–1,000 °C). Taken together, however, the extent of vitrification and the firing temperature reflect the technological capabilities of the ancient potters with respect to both their ability to achieve the necessary temperatures and their understanding of the refractory properties of the clay used. In this respect, therefore, the examination of ancient pottery with an SEM is more valuable than an estimate of the firing temperature by itself,

such as can be obtained either by studying those minerals altered during firing^{3,4} or by thermal expansion measurements⁵.

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Temperature-independent relaxation in a lamellar block copolymer

It has long been assumed that all processes giving rise to stress relaxation in high polymers are very dependent on temperature. The peak in mechanical or dielectric loss factor ($\tan\delta$) can be used to characterise the most probable relaxation time of a high polymer solid. The temperature locus of this relaxation time is described by a simple Arrhenius-type law for low temperature, glassy state processes¹ and by the Williams, Landel and Ferry expression² for ' T_g ' processes. We now report results for an elastomer exhibiting a unique relaxation process which remains essentially constant in position and magnitude over a temperature range of more than 100 K.

The block copolymer used was a poly(α -methylstyrene-*b*-dimethylsiloxane) prepared with 'star' geometry $(AB)_4X$, where A represents a poly(α -methylstyrene) block, B a poly(dimethylsiloxane) block and X is a tetrafunctional coupling atom. This polymer was synthesised by Dr D. Jones, Dow Corning Company, by sequential anionic copolymerisation³. The product contained 37.5% (w/w) poly(α -methylstyrene), molecular weight 9,000, with the molecular weight of the B block 15,000. In common with other block copolymers, different morphologies can be achieved by differing the physical treatment⁴. In the present case lamellar morphology could be generated by compression moulding a sheet (523 K, 13 MPa (130 bar)) with considerable flow in the plane of the sheet or by slow casting from benzene on a mercury surface. Dynamic mechanical measurements were carried out either in bending geometry (bars $\approx 20 \times 10 \times 2$ mm) to give Young's modulus (E') or in shear sandwich geometry (cubes with side 2 mm) to give the rigidity over wide ranges of temperature and frequency on a slightly modified version of a phase- and amplitude-measuring mechanical spectrometer previously reported^{5,6}.