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DETERMINING THE FIRING TEMPERATURE OF LOW-FIRED ANCIENT POTTERY: AN EXAMPLE FROM THE DONGHULIN SITE, BEIJING, CHINA*

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*The traditional thermal expansion method using a dilatometer fails to accurately determine the original firing temperatures of low-fired ancient pottery. For this reason, we have developed an improved method of determining firing temperatures for low-fired pottery. This paper explains the theory of the improved method and presents the reasonably satisfactory results obtained on ancient pottery from the Donghulin site (*c. *10 000 BP). The method and the results are very important for the study of ancient pottery culture and clay moulds used for bronze casting.*

KEYWORDS: FIRING TEMPERATURE, LOW-FIRED POTTERY, DILATOMETER, DONGHULIN

INTRODUCTION

Pottery is one of the most common classes of artefacts found in archaeological contexts, the emergence of which was one of the most important accomplishments for humankind after mastering the use of fire. Archaeologists conduct frequent studies of ancient pottery to reconstruct past human activity (Kaiser and Lucius 1989).

The process of pottery-making contains a wealth of scientific and archaeological information. Part of the process of pottery production involves the firing of the clay. Because a majority of pottery remains are sherds and only a few of the remains can be restored to their original condition, it is difficult to obtain information about the ancient pottery-makers through the traditional study of ceramic typology alone. However, an understanding of the techniques of pottery manufacture is particularly important when we carry out studies of early pottery. With this understanding, a quantitative, precise method to determine the sintering temperature and firing atmosphere of early pottery will improve our technical understanding of ancient human society and related human behaviour. In particular, being able to determine the firing temperature of the clay will improve our understanding of how the craft of pottery manufacture evolved (Wang and Liu 2005).

There have been numerous attempts to determine the firing temperatures of ceramics. One of the first methods to be employed was X-ray diffraction (XRD), which identified the residual

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minerals in pottery by their phase and quantity (Maggetti 1982). Subsequently, petrographic analysis, scanning electron microscopy (SEM) and other techniques were utilized (Maniatis and Tite 1981; Wagner and Wagner 2004; Mangone *et al*. 2009). With these techniques, one could observe the sintering process and estimate the firing temperature of the ceramics. However, the methods are not accurate enough for most archaeological studies because their methodologies are indirect. One of the most recent methods is the thermal expansion method, which measures the physical properties of pottery relative to temperature (Tite 2008). Thermal expansion is now the most common method for determining the firing temperature of ceramics, because it is a more direct and precise technique. A new method based on magnetic susceptibility has been reported by Rasmussen *et al*. (2012).

The technique for determining the firing temperatures by thermal expansion of ancient ceramics was originally developed by Roberts (1963) and further refined by Tite (1969). The technique that Roberts and Tite developed is based on two assumptions. First, when clay is fired, shrinkage will occur with various sintering processes. If a previously fired clay ceramic is reheated slowly from room temperature upwards, it exhibits a normal reversible thermal expansion until it reaches the original firing temperature. Second, when the reheating temperature exceeds the original firing temperature, the ceramic begins to contract, since there is an irreversible shrinkage associated with the resumption of sintering. The temperature at which expansion ends and contraction occurs should therefore provide an estimate of the original firing temperature.

The firing temperature assumed by the thermal analysis instrument is determined by examining a thermal expansion curve. The thermal expansion curve is the relative change in sample length affected by the change in temperature. The relative change rate of the sample length is expressed as $\Delta L/L_0$ (ΔL is the length of change and L_0 is the original length of sample). On the other hand, firing research shows that once the firing temperature of a ceramic material achieves the vitrification temperature (usually in the range from 700 to 950°C), a new glass phase begins to occurs in the interior body and is accompanied by volume shrinkage. The vitrification temperature depends on the concentration of fluxing agents, such as Na_2O, K_2O, Fe_2O_3, CaO and so on, in the material. The shrinkage effect is related to the temperature after maintaining the ceramic at fixed temperature for a certain length of time.

A problem with this method is that if the original firing temperature of pottery is below 900°C, then the technique does not accurately estimate the firing temperature. This was pointed out originally by Tite (1969). The reason is that when the original firing temperature is lower than the temperature at which the glass phase begins to develop, the sample cannot form a new glass phase within the body of the sample. As a result, there is no additive volume shrinkage, and the measured thermal expansion curve does not provide information on the original firing temperature.

In this paper, we propose an improved method to determine firing temperatures in low-fired ceramics (< 900°C). We make use of both simulated and ancient pottery samples to demonstrate our methodology.

BACKGROUND

Prehistoric archaeological research, as it relates to technology and early human behaviour, is often concerned with pottery production. Ethnographic evidence shows that early pottery firing temperatures were generally low due to technological limitations. Current archaeological methods do not allow detailed analysis of such low firing temperatures. However, the improved

technique of thermal expansion proposed here will allow archaeologists to determine the low firing temperatures of prehistoric archaeological ceramics accurately.

The earliest pottery emerged in the world during the transition from the Pleistocene to the Holocene, at about 18 000–9000 BP. Pottery originated almost simultaneously in several different areas, including northern and southern China (Zhao and Wu 2000), Japan (Tsutsumi 2000), the Russian Far East (Zhushchikhovskaya 1997), Western Asia (Moore 1995) and North Africa (Angela 1995). These six areas were the main pottery-originating centres of the world. Differences in pottery vessel shapes and manufacturing methods existed from the beginning. The characteristics of pottery in each region can help to explain the differences in manufacturing practices in each region.

In the 1990s, early pottery was found in Beijing and the surrounding areas of Nanzhuangtou, Zhuannian and Donghulin (Wang 2007). The cultural relics discovered are between 9000 and 12 000 years old, and the sites provide valuable information for early pottery studies. Among the above-mentioned sites, Donghulin is very representative of northern China. A large quantity of cultural remains, including pottery, stone tools, bone tools, and animal and plant remains, were found at the site. Archaeologists also found tombs, ash heaps and the remains of residences. Discoveries of sites dating to around 10 000 BP are relatively rare and precious on a world scale.

In this study, we selected the pottery from the Neolithic period Donghulin site as the location for our archaeological samples. The site is located west of the Mentougou District, along the northern bank of the Qing Shui River. The site has been excavated four times during the period from 2001 to 2007. The cultural remains from the site have been radiocarbon dated to between 9000 and 12 000 years BP (Zhao *et al*. 2003; School of Archaeology and Museology of Peking University *et al*. 2006). These dates prove that the Donghulin site is one of the earliest Neolithic sites and therefore one with the earliest known locations for pottery production.

MATERIALS AND METHODS

The method

The dilatometry (DIL) device is currently the most accurate device for measuring change in the dimensions of materials caused by thermal expansion. The DIL allows highly precise temperature (0.3°C) control with negligible sample strain. This high degree of temperature sensitivity allows the device to determine the firing temperature of pottery more accurately than other traditional devices.

The dilatometer used for this research was a model DIL402C, made by NETZSCH-Gerätebau GmbH (Selb, Germany). It is designed with an Invar measurement system, a high-resolution displacement transducer and comprehensive thermostatic control. The instrument offers the highest degree of accuracy, reproducibility and long-term stability for temperatures up to 1600°C. Proteus™ software licensed with the dilatometer was used to carry out the measurements and evaluate the resulting data.

Samples were placed on an Al_2O_3 holder and heated at a rate of 5°C min^{-1} in a nitrogen gas atmosphere. The sampling rate was 60 pts min^{-1} or 12 pts k^{-1}.

Before testing the samples, the system error was adjusted. If the system error is not corrected in advance, the thermal expansion curve will show both the rate of sample change as well as the rate of change of the machine's support system. The error can be corrected by establishing a baseline thermal expansion curve for a standard material and then comparing the unknown sample's thermal expansion curve to the baseline (Zhang *et al*. 2008). Because the equipment

uses a frame and pushrod made of aluminium oxide, we selected aluminium oxide as the standard sample. All samples, as well as the standard samples, were placed on the holder with a thin wafer of alumina between the samples and the pushrod. The alumina prevents adhesion between the pushrod and the pottery samples. Within the Proteus software, the correction measurement option was selected so that the machine could correct the error internally.

The XRD method was utilized to verify our method of determining the low firing temperature of ancient pottery by the DIL machine. X-ray diffraction identifies the crystalline phases dispersed in the glass matrix of the sample by utilizing a Rigaku X-ray Diffractometer (RINT-2000) with Cu–K_α ($\lambda = 1.5406$ Å). Individual samples consisted of 500 mg of material pressed into a glass holder after being ground in an agate mortar to 325 mesh (<44 mm). The operating conditions for the XRD were a voltage of 40 kV, a current of 40 mA, a divergence slit of 1°, an anti-scattering slit of 1° and a receiving slit width of 0.15 mm. Samples were scanned over an angular 2θ range from 5° to 75°.

Preparation of samples

The raw material for the simulated clay specimens was collected from the Donghulin site near Beijing, China. The clay material was separated into multi-sections and each section was formed into a block ($1.5 \times 0.5 \times 0.5$ cm^3). The same process was performed on the archaeological pottery sherds after all external contamination was removed. Prior to measurement, the clay specimens and pottery sherds were heated to 120°C to remove all atmospheric water. A high-precision electric furnace was used to individually heat the clay blocks over a temperature range from 400 to 1000°C, to make them pottery-like.

The firing temperature should represent the temperature at which the body has stabilized all physical and chemical changes. If the temperature reaches a peak at which the temperature drops suddenly, the pottery firing temperature will be lower than the highest temperature. Therefore, it is necessary to identify an appropriate holding time for the body of the ceramic to stabilize.

For our experiments, both the simulated and archaeological samples require measurement of precise reheating temperatures. If the furnace temperature control system is unreliable, the results will be difficult to repeat.

Identifying the appropriate heating time is one of the keys to accurately determining the firing temperature. As shown in Figure 1, the thermal expansion curve of simulated pottery has been heated to 500°C with a holding time of 15 h. At the beginning of the heating cycle, slow shrinking occurs. After keeping the temperature fixed at 500°C for 180 min, sample contraction becomes stable. By means of this observation, the recommended holding time is 3 h.

RESULTS

Using the traditional method

To demonstrate that low-fired pottery cannot be accurately measured by the traditional DIL method, the fired blocks were put into the DIL device and tested by the traditional method. The results are shown in Figure 2.

If the firing temperature is estimated by the appearance of shrinkage, then the results shown in Figure 2 suggest that the original firing temperature was between 800 and 900°C regardless of the original firing temperature. This phenomenon is due to the fact that shrinkage associated with vitrification of pottery always occurs between 800 and 900°C. Figure 3 shows a curve for pottery

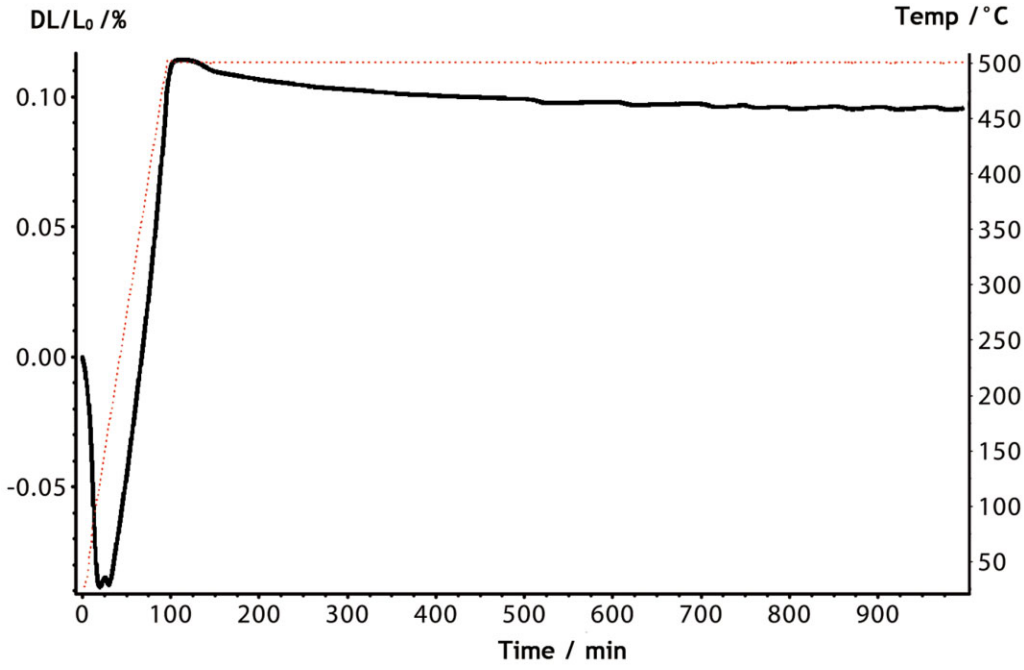

Figure 1 *Results from the heating of a pottery sample at a fixed temperature of 500°C for 15 h.*

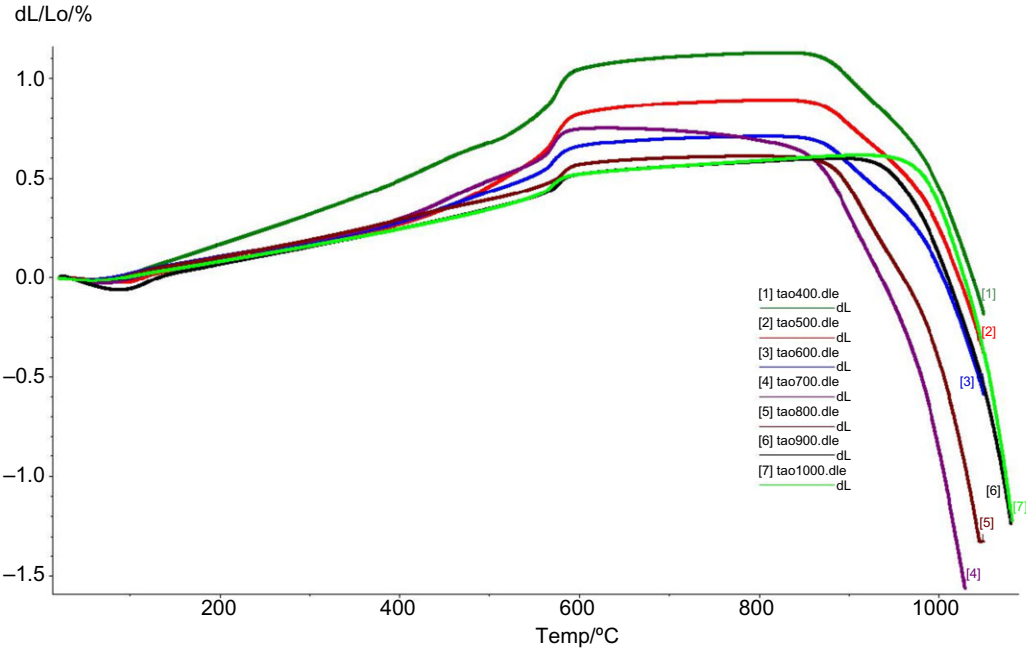

Figure 2 *Thermal expansion curves for simulated pottery samples.*

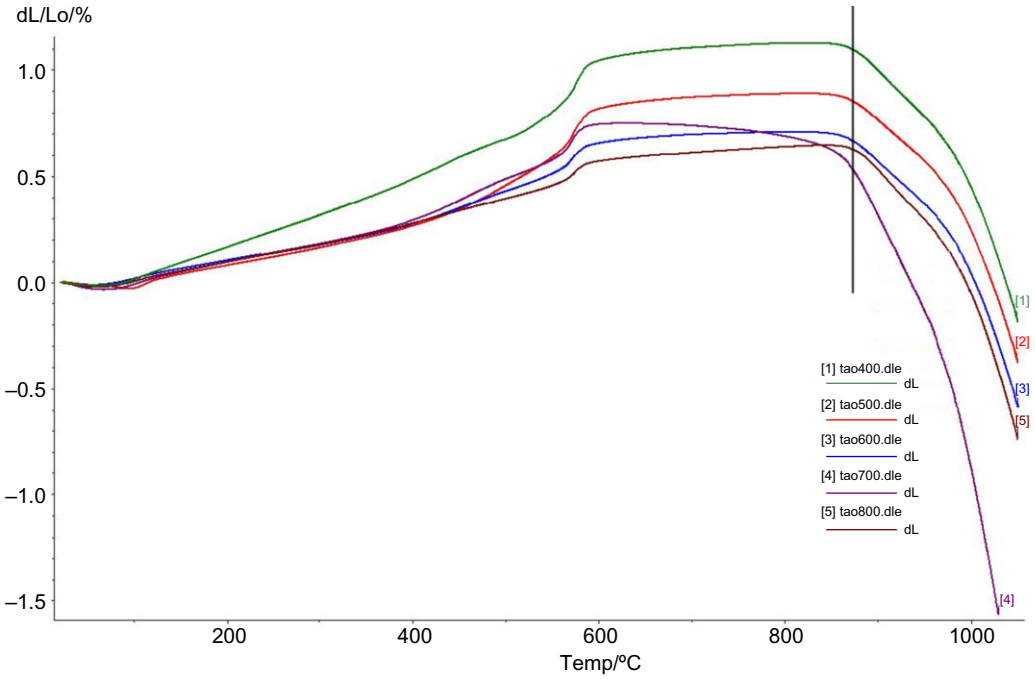

Figure 3 *Thermal expansion curves for simulated pottery samples using low firing temperatures.*

in which the original firing temperature was below 900°C. It is much easier to identify the inflection point on Figure 3. Therefore, the curve inflection point as determined by the traditional method does not accurately determine the firing temperature for low-fired pottery.

Validating the improved method on low-fired ceramics

While the original firing temperature of a ceramic is lower than its vitrification temperature, there is mainly solid state sintering and hardly any formation of a new glass phase during the firing process (Rahaman 2003). When the pottery is reheated to temperatures lower than or equal to its original firing temperature, its structure will generally not be affected. Once the reheating temperature exceeds its original firing temperature and is held stable for a sufficient time, the density of the pottery body will be increased, but its thermal expansion curve will maintain its original position. This is because the thermal expansion curve is drawn according to its former density. Subsequently, when the pottery is heated again, the new thermal expansion curve will move to a lower position regardless of whether the reheating temperature is higher or lower than the original firing temperature. On the basis of this principle, the original firing temperature of pottery can be determined by gradually raising the temperature.

To validate the assumption that low firing temperatures can be estimated from the thermal expansion curve, a validation experiment was designed.

In this validation experiment, the vitrification temperature of the clay samples is around 870°C. Therefore, four clay specimens were fired to temperatures of 500, 600, 700 and 800°C, respectively. Each sample was then inserted into the DIL machine and reheated at temperatures starting 50°C lower than the original firing temperature. When the measuring temperature reaches the

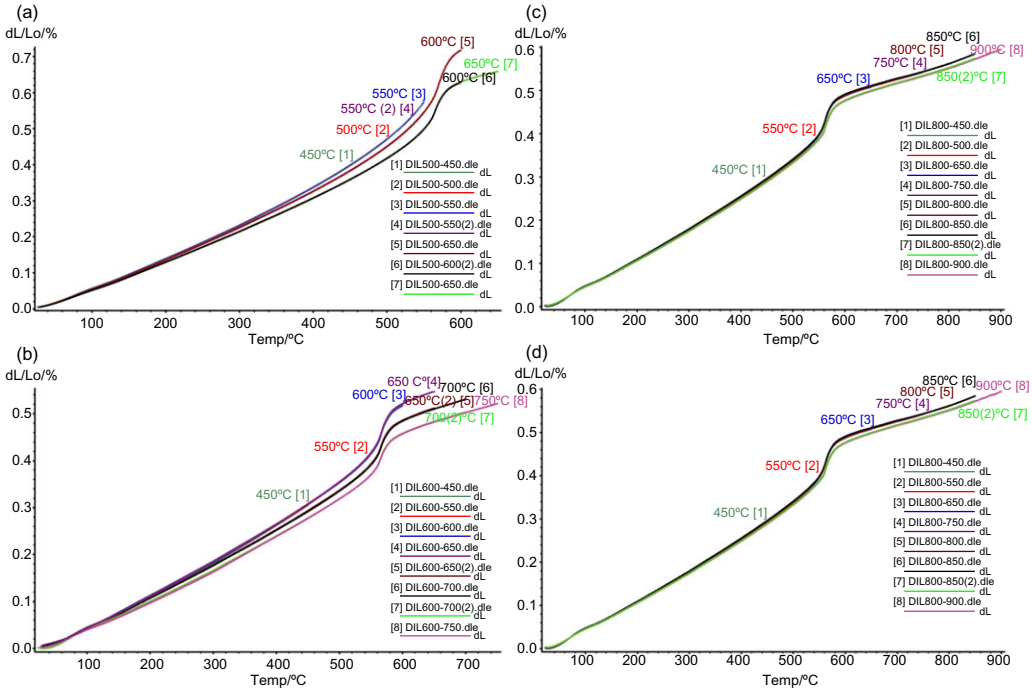

Figure 4 *Thermal expansion curves for reheated simulated samples. The original firing temperatures were as follows: (a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C. In the figures, the first number represents the original firing temperature and the other numbers represent the reheating temperatures used.*

maximum, it should be held at this temperature for at least 3 h before the samples are cooled to room temperature. Next, the sample is reheated to a temperature that is 50°C higher than the last measurement. Every measurement step is recorded by the Proteus software and the thermal expansion curve is drawn automatically from the experimental data. Once the reheating temperature exceeds 100 or 150°C of its original firing temperature, measurements are discontinued.

Figure 4 (a) shows an example in which a simulated clay sample was heated to an original firing temperature of 500°C. When the sample is reheated to 450°C and 500°C, the curves almost completely overlap. When the temperature reaches 550°C for the first time, the curve is still similar to the highest firing temperature of 500°C according to its former firing history, so the curves still coincide. When the temperature reaches 550°C for the second time, the sample's thermodynamic shrinkage rate decreases. As a result, the expansion curve moves downwards. Here, it can be assumed that the reheating temperature of the second to last time has exceeded the original firing temperature. The same measurement steps can be used for samples with original firing temperatures of 600, 700 and 800°C. The similar results are shown in Figures 4 (b)–(d).

Applying the improved method to archaeological samples

Four samples from the Donghulin site were selected for measurement. The sample IDs are T3⑦-1504, T8⑤-276, T8⑤-278 and T9⑧-385. For convenience, we refer to simplified IDs

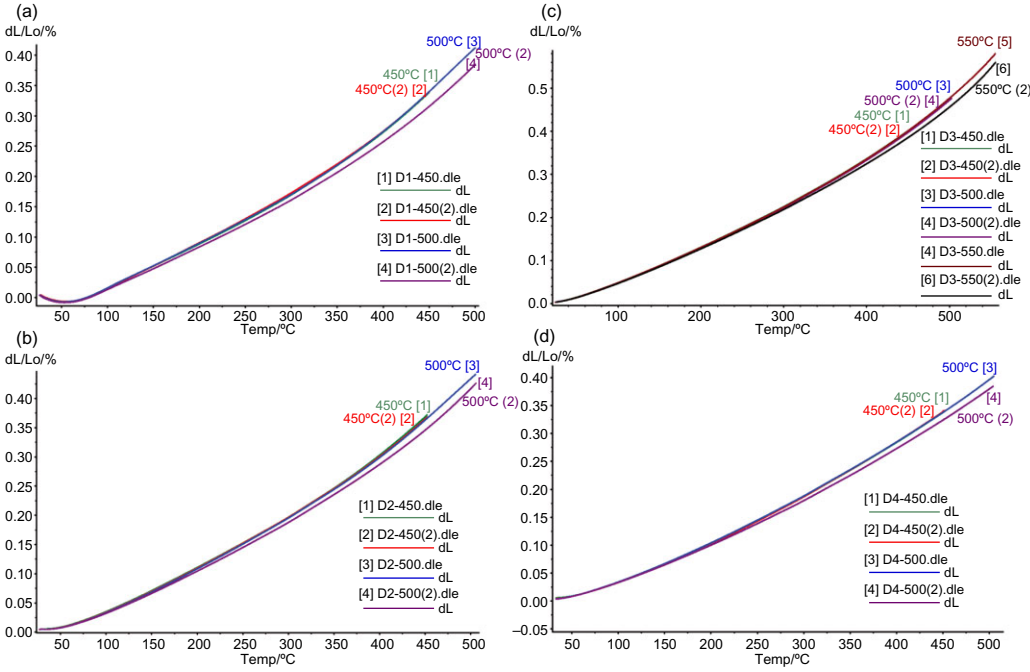

Figure 5 *Thermal expansion curves for archaeological samples from Donghulin: (a) sample D1; (b) sample D2; (c) sample D3; (d) sample D4.*

instead: T3⑦-1504 as D1; T8⑤-276 as D2; T8⑤-278 as D3; and T9⑧-385 as D4. In accord with the above experiments on simulated samples, the archaeological samples were measured using our new method.

First, all samples were dried at 120°C for 3 h and heated to 450°C. The samples were held at this temperature for 3 h and then cooled down to room temperature. Next, the samples were reheated at temperatures 50°C higher than the previous measurement. Every measurement step was recorded by the Proteus software and its thermal expansion curves were drawn automatically from the experimental data. When the thermal expansion curve moved to a lower position, the measurement on a particular sample was discontinued. The original firing temperature of the sample was estimated to lie between the reheating temperature of the second and third reheatings.

The results are shown in Figure 5. On the basis of observing the thermal expansion curves, the original firing temperature of samples D1, D2 and D4 should lie between 450 and 500°C and the firing temperature for D3 should lie between 500 and 550°C. To verify our observations, we also used X-ray diffraction to analyse the samples. Figure 6 shows the results of the XRD analyses for samples D1 and D3. The XRD results show that the samples contain quartz, feldspar and clay. The diffraction peaks of quartz are high and narrow, which means that there are still a large number of quartz crystals within the sample. This means that the original firing temperature was not high. These results are consistent with the results obtained from our proposed new method.

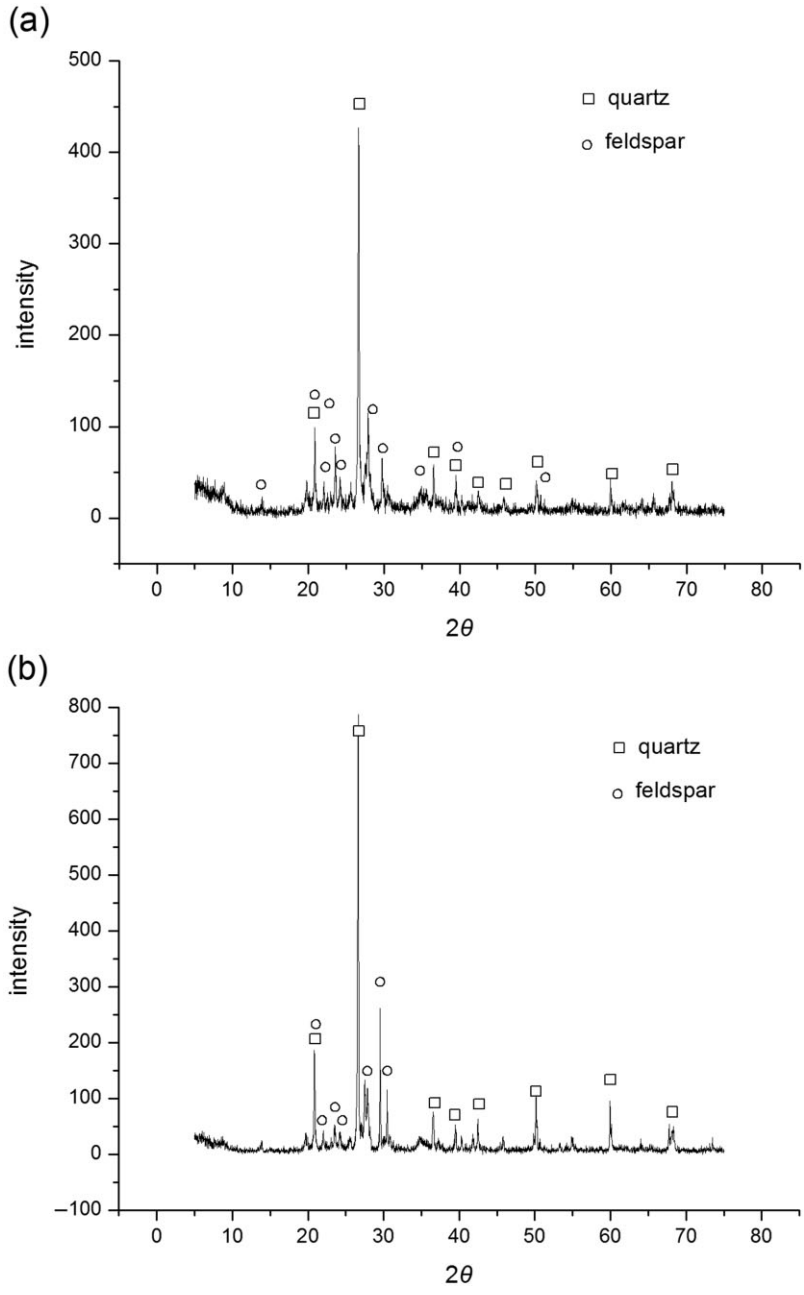

Figure 6 *The XRD results for (a) sample D1 (T3⑦-1504) and (b) D3 (T8⑤-278).*

CONCLUSIONS

On the basis of our experiments with simulated and archaeological samples, we are able to draw the following conclusions:

(1) The improved thermal expansion method can be used to accurately determine the original firing temperature of low-fired pottery when the original firing temperature is lower than the vitrification temperature.

(2) The original firing temperatures for the four pottery sherds excavated from the site of Donghulin lay between 450 and 550°C. This proves that the firing techniques used to produce pottery at Donghulin at around 10 000 BP involved low temperatures.

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