GEOCHRONOMETRIA 40(4) 2013: 317-321
DOI 10.2478/s13386-013-0122-9

Available online at
www.springerlink.com

FIRING TEMPERATURE OF A CLAY CORE SAMPLE IN A BRONZE TRIPOD FROM DAXINZHUANG SITE IN CHINA USING TL TECHNIQUES

YOUJIN WU[1], ZHENGYAO JIN[1, 2], ANCHUAN FAN[1] and HUI FANG[3]
[1]*USTC Archaeometry Laboratory, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China*
[2]*National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China*
[3]*The School of History and Culture, Shandong University, Jinan, Shandong 250100, PR China*

Received 30 January 2013 Accepted 1 July 2013

Abstract: In this paper, we studied the thermal history of a clay core sample from one leg of a bronze tripod unearthed at Daxinzhuang Site, Shandong, China. The properties of the luminescence signals of quartz depend on the maximum temperature at which the quartz was annealed in the past. We examined the feasibility of measuring the thermoluminescence (TL) sensitivity change of quartz for exploring the firing temperature of archaeological materials. The sensitization factor of the 110°C TL peak (S_2/S_1) and the ratio of the 210°C TL peak to the 110°C TL peak at different annealing temperatures were utilized to unveil the firing temperature in the clay core sample. The firing temperature of the clay core sample was approximately 700°C-800°C, proving the clay core has been fired. This result proved that the clay core has been fired by human agencies and indicated on the temperature of the clay core in drying and firing given by the foundry workers before the actual casting step.

Keywords: firing temperature, thermoluminescence, archaeological sample, clay core sample.

1. INTRODUCTION

Thermal treatment has a profound influence on the luminescence properties of quartz. There are large differences in the sensitivity of the 110°C TL glow peak signal and the optically stimulated luminescence (OSL) signal between unheated and heated quartz (Aitken and Smith, 1988; Bøtter-Jensen and Duller, 1992). The sensitivity change experienced by a sample since antiquity is primarily governed by the thermal treatment during manufacturing or thereafter during its lifetime (Roque *et al.*, 2004). For excavated bronzes, the firing temperature of ceramic cores or moulds before the casting processes can provide a basis for understanding the ancient casting technique.

Attempts have been made to estimate the firing temperatures of quartz (Sunta and David, 1982; Watson and Aitken, 1985; Koul *et al.*, 1996; Lahaye *et al.*, 2006) and flint (Melcher and Zimmerman, 1977; Göksu *et al.*, 1989; Godfrey-Smith and Iiani, 2004) based on the changes of thermoluminescence (TL) sensitivity. In recent years, studies focused on the possibility of monitoring the sensitivity changes for both the TL and the OSL signals of quartz to determine the firing temperature (Polymeris *et al.*, 2007; Koul and Chougaonkar, 2011; Jin *et al.*, 2012). Polymeris *et al.* (2007) suggested that techniques based on both TL and OSL signals would provide an assessment of the firing temperatures. The TL glow curves showed different shapes for the annealing temperature above the firing temperature, particularly the 210°C TL peak. Using the sensitivity of 210°C TL glow peak and

Corresponding author: Z. Y. Jin
e-mail: zyjin@ustc.edu.cn

ISSN 1897-1695 (online), 1733-8387 (print)

sensitization characteristics of 110°C TL peak and OSL, Jin *et al.* (2012) studied the firing temperature of archaeological sand. Their results suggested that a combination of luminescence sensitivity, sensitization factor and TL glow curve can provide a new method for unveiling firing temperatures of archaeological ceramics. They have successfully used the natural quartz of industrial interest presenting a high degree of purity (99.8% of SiO_2, according to Sinopharm Chemical Reagent industry data) as a standard sample (hereinafter referred to as 'SQ' sample) to determine the firing temperature of quartz sand from archaeological materials.

The present work investigates the sensitization characteristics of the 110°C TL peak and TL glow curve of the samples heated at different temperatures to estimate the firing temperature of the clay core sample in a bronze tripod from the Daxinzhuang Site.

2. SITE AND SAMPLES

The Daxinzhuang site is in the southeast of Daxinzhuang Village, Wangsheren Town, Licheng District of Jinan City, Shandong Province. To the south of the site is the piedmont of the Tai-Yi mountain, and Xiaoqinghe is less than 3 km to the north of the site (**Fig. 1**). The Daxinzhuang site is one of the most important Shang settlements in eastern China (report from the Centre for East Asian Archaeology Studies of Shandong University, 2008). The rapid emergence of this town provided the first indication of a Shang population intrusion into the coastal region of Shandong. The discoveries of the Shang oracle bone inscriptions outside of the Late Shang capital Anyang and the early Shang bronzes add some rare material for historical and sociological research during the Shang period. In this study, a clay core sample in one bronze tripod which had not been removed by human agencies (**Fig. 2**) from the Daxinzhuang Site was investigated (report from Department of Archaeology, Shandong University and Shandong Provincial Institute of Cultural Relics and Archaeology, 2010). According to the stylistic characterics of the bronze tripod, the age of the clay core sample may be from a period of 770-256 BC The archaeological quartz sample (hereinafter referred to as 'AQ' sample) was extracted from the clay which be sampled from the centre of the clay core.

Fig. 1. *The location of Daxinzhuang site which located in the south of Xiaoqinghe and in the north of the Tai-Yi mountain.*

3. EXPERIMENTAL DETAILS

Sample preparation was carried out under subdued red light in the Archaeometry Laboratory, University of Science and Technology, China. The quartz sample (AQ) was processed using conventional sample preparation techniques (sieving, HCl, H_2O_2, HF etching and re-sieving) to obtain 90-150 μm quartz grains (Jin *et al.* 2012). The purity of the quartz extracts was confirmed by infrared-testing (the ratio of the infrared stimulated luminescence (IRSL) to the blue light stimulated luminescence (BLSL) ratios is less than 1%).

The AQ and SQ samples were thermally annealed in an electric oven at various temperatures using a linear heating rate of 5°C/s for two hours followed by a slow cooling down to room temperature (cooling rate: less than 2°C/min). The SQ sample was annealed to temperatures of 300°C, 400°C, 500°C, 530°C, 550°C, 580°C, 600°C, 630°C, 650°C, 680°C, 700°C, 730°C, 750°C, 780°C,

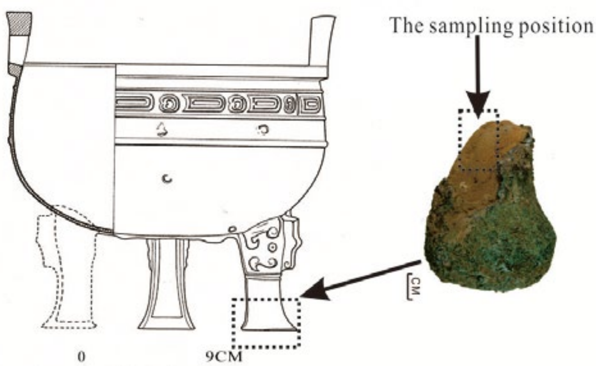

Fig. 2. *The clay core sample in a bronze tripod (04JDM4:10) from Daxinzhuang Site, Shandong, China. The bronze tripod line graph is not the artifacts unearthed in Daxinzhuang Site but is only used to refer to the bronze artifact's type. The archaeological quartz grains were extracted from the clay sampled from the centre of the clay core.*

800°C, 830°C, 850°C, 880°C, 900°C in order to set a standard reference. The AQ sample was annealed to temperatures of 500°C, 600°C, 700°C, 800°C and 900°C.

All luminescence measurements were carried out with an automated Risø TL/OSL-DA-20 system (Bøtter-Jensen *et al.*, 2003), equipped with 28 blue LEDs (470±20 nm) operating at 80% power (~40 mW cm^{-2}). It contains an attached $^{90}Sr/^{90}Y$ beta source with a dose rate of 0.1636 Gy/s on quartz grains on stainless discs. The filters are 7.5 mm thick U-340 filters. Six aliquots for each annealing temperature were measured.

In the 110°C TL measurement experiment, each aliquot was heated up to 260°C after a given beta dose of 4.81 Gy. The aliquot was then bleached and heated to 500°C to eliminate signals. Such procedures were repeated two times for each aliquot. The sensitivity S_i, which is based on the 110°C TL peak, was recorded in the preheating procedure. The first measurement without the 500°C annealing in the equipment yielded S_1. The procedure as follows:

1) Administer a test dose of 4.81 Gy;
2) Heat to 260°C at 5°C/s and record the intensity of 110°C TL peak (S_1);
3) Bleach by Blue-LED at 125°C for 40 s;
4) Heat to 500°C to eliminate signals;
5) Repeat steps 1 to 4 to record the intensity of 110°C TL peak (S_2).

Another group of aliquots of the AQ sample were used to study the behavior of the TL signal after annealing at various temperatures. The TL glow curves were recorded up to 500°C using a heating rate of 5°C/s. The given beta dose was 48.1 Gy. The ratio of the TL peak heights of 210°C to that of the 110°C ($S_{210°C}/S_{110°C}$) of the AQ samples was obtained after annealing to 500°C, 600°C, 700°C, 800°C and 900°C. The procedure as follows:

1) Administer a test dose of 48.1 Gy;
2) Heat to 500°C at 5°C/s to record the TL glow curves;
3) Repeat steps 1 and 2 to record the TL glow curves ($S_{210°C}/S_{110°C}$).

4. RESULTS AND DISCUSSIONS

Variation in the sensitization factor (S_2/S_1) of 110°C TL peak

The sensitivity of the 110°C TL peak shows a significant difference between the clay core samples and standard quartz. It is consistent with the difference between heated archaeological samples and unheated quartz reported by other authors (Aitken and Smith, 1988; Bøtter-Jensen and Duller, 1992). We infer that the clay core sample was heated in the past for casting. The sensitization factor (S_2/S_1) is the ratio of the 110°C TL peak intensities annealed between the second and first TL glow curves to 500°C. The variation of the sensitization factor (S_2/S_1) of the 110°C TL peak of the SQ samples was reported (Jin *et al.*, 2012). Comparing S_2/S_1 ratios of the AQ sample with the SQ sample suggests that the factor of the AQ sample correspond to three firing ranges of the SQ sample (**Fig. 3**), i.e. 500-600°C, 700-800°C and above 850°C. Based on those results, we selected the annealing temperatures of 500°C, 600°C, 700°C, 800°C and 900°C to study the pattern of the TL signal of the AQ samples.

Variation of the pattern of the TL signal

In order to unveil the firing temperature of the clay core sample in the past, the changes of the 210°C TL peak of the AQ samples annealed at 500°C, 600°C, 700°C, 800°C and 900°C after the OSL bleaching were investigated. As can be seen in **Fig. 4**, the TL glow curves of the AQ samples annealed at 500°C, 600°C, 700°C exhibit no significant changes. The TL glow curves attain a different shape when the AQ samples were annealed at 800°C and 900°C. The 210°C TL peak of the AQ samples annealed at 800°C and 900°C increase distinctly.

To explore this further, we compared the ratio of the 210°C TL peak to the 110°C TL peak. The normalized ratio of the 210°C TL peak height to the 110°C TL peak height ($S_{210°C}/S_{110°C}$) for the AQ samples versus the annealing temperature is presented in **Fig. 5**. The ratio of $S_{210°C}/S_{110°C}$ remained stable for annealing temperatures up to 700°C, but the ratio ($S_{210°C}/S_{110°C}$) increases abruptly when the annealing temperature exceeds 800°C. Annealing at the temperature of 800°C enhances the ratio by a factor 14. The equivalent firing temperature range for the AQ samples from the clay core is estimated to be at around 700°C less than 800°C.

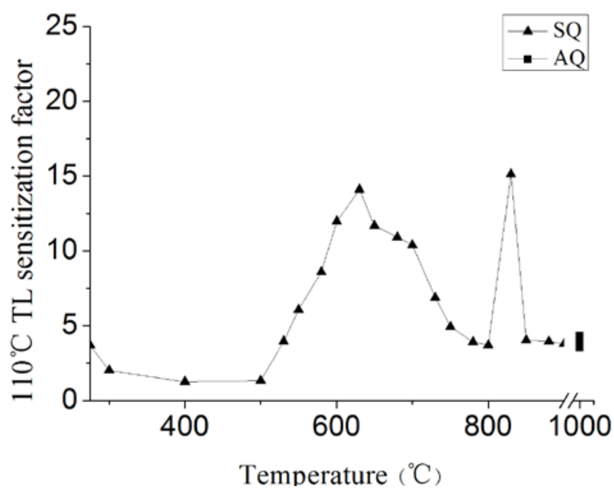

Fig. 3. *Curves for the variation in the sensitization factor (S_2/S_1) of the 110°C TL peak for the SQ samples annealed at different temperatures and the ambient temperature of AQ samples with a beta dose of 4.81 Gy. The graph shows the ratio of the 110°C TL peak between the second and first TL glow curves to a maximum temperature of 500°C. For the unheated AQ samples, six aliquots were used.*

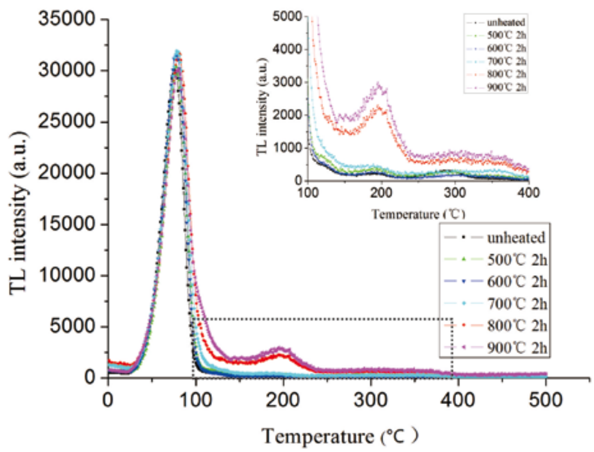

Fig. 4. *The TL glow curves of the AQ samples annealed at different temperatures. Glow curves were obtained for various annealing temperatures with heating to a maximum temperature of 500°C using a linear heating rate of 5°C/s and normalized to the intensity of 110°C TL peak. Inserted plot shows the TL glow curves of the AQ samples annealed at different temperatures from 100°C to 400°C.*

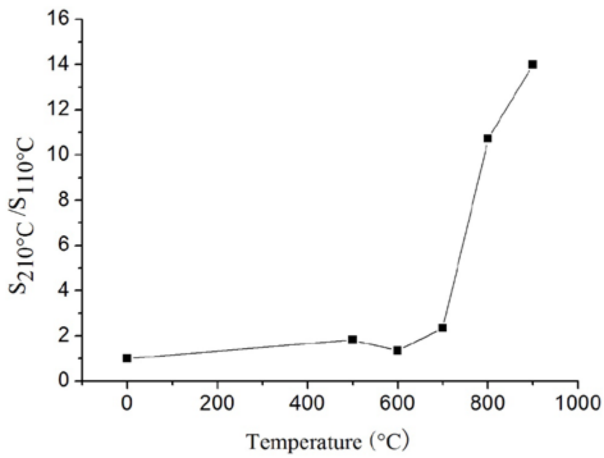

Fig. 5. *A plot of the normalized ratio of the 210°C TL peak height to the 110°C TL peak height ($S_{210°C}$ /$S_{110°C}$) against the annealing temperature on quartz grains separated from the clay core (AQ) sample. The ratio of $S_{210°C}$ /$S_{110°C}$ is normalized to the ambient temperature of the AQ sample.*

5. CONCLUSION

The sensitization characteristics of the 110°C TL peak and the pattern of the TL signal change as a function of the annealing temperature. The TL signal suggests that the clay core sample had been heated in the past. The equivalent firing temperature range is 700-800°C. This result proved that the clay core has been fired by human agencies and indicated on the temperature of the clay core in drying and firing given by the foundry workers before the actual casting step.

It is possible that a combination of the sensitization factor of the 110°C TL peak (S_2/S_1) and the pattern of the TL signal may be applied as a new method for firing temperature estimation. The variation in the sensitization factor of the 110°C TL peak (S_2/S_1) could indicate the range of the firing temperature. The behavior of the entire TL glow curve could provide more information in determining the firing temperature.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (NSFC, No. 41073004) and the Programme of Introducing Talents of Discipline to Universities (111-2-09). We are grateful to Prof. James Burton for his help to polish the language of our article. We also thank the anonymous reviewer for their valuable comments and constructive suggestions.

REFERENCES

Aitken MJ and Smith BW, 1988. Optical dating: recuperation after bleaching. *Quaternary Science Reviews* 7(3-4): 387-393, DOI 10.1016/0277-3791(88)90034-0.

Bøtter-Jensen L, Andersen CE, Duller GAT and Murray AS, 2003. Developments in radiation, stimulation and observation facilities in luminescence measurements. *Radiation Measurements* 37(4-5): 535-541, DOI 10.1016/S1350-4487(03)00020-9.

Bøtter-Jensen L and Duller GAT, 1992. A new system for measuring OSL from quartz samples. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* 20(4): 549-553, DOI 10.1016/1359-0189(92)90003-E.

Department of Archaeology, Shandong University and Shandong Provincial Institute of Cultural Relics and Archaeology, 2010. Tomb No.139 of the Shang Dynasty at Daxinzhuang Site, Jinan city. *Kaogu* 10: 3-6 (in Chinese).

Godfrey-Smith DI and Ilani S, 2004. Past thermal history of goethite and hematite fragments from Qafzeh Cave deduced from thermal activation characteristics of the 110°C TL peak of enclosed quartz grains. *Rev Archéométrie* 28: 185-190 (in French).

Goksu HY, Weiser A and Regulla DF, 1989. 110°C TL peak records the ancient heat treatment of flint. *Ancient TL* 7: 15-17.

Jin ZY, Wu YJ, Li G, Fan AC, Cheng GS and Yan LF, 2012. Luminescence determination of firing temperature of archaeological pure sand related to ancient Dian bronze casting, China. *Quaternary Geochronology* 10: 387-393, DOI 10.1016/j.quageo.2012.04.010.

Koul DK and Chougaonkar MP, 2011. An attempt to estimate firing temperature using OSL pre-dose sensitization of quartz. *Geochronometria* 38(3): 217-222, DOI 10.2478/s13386-011-0034-5.

Koul DK, Singhvi AK, Nambi KSV, Bhat CL and Gupta PK, 1996. Feasibility of estimating firing temperature using the 110°C peak of quartz. *Applied Radiation and Isotopes* 47(2): 191-195, DOI 10.1016/0969-8043(96)82846-6.

Lahaye C, Godfrey-Smith DI, Guibert P and Bechtel F, 2006. Equivalent thermal history (H_E) of ferruginous sandstones based on the thermal activation characteristics of quartz. *Radiation Measurements* 41(7-8): 995-1000, DOI 10.1016/j.radmeas.2006.04.021.

Melcher CL and Zimmerman DW, 1977. TL determination of heat treatment of chert artifacts. *Science* 197, 1359-1362, DOI 10.1126/science.197.4311.1359.

Polymeris GS, Sakalis A, Papadopoulou D, Dallas G, Kitis G and Tsirliganis NC, 2007. Firing temperature of pottery using TL and OSL techniques. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 580(1): 747-750, DOI 10.1016/j.nima.2007.05.139.

Roque C, Guibert P, Vartanian E, Vieillevigne E and Bechtel F, 2004. Changes in luminescence properties induced by thermal treatments; a case study at Sipan and Trujillo Moche sites (Peru). *Radiation Measurements* 38(1): 119-126, DOI 10.1016/S1350-4487(03)00249-X.

Sunta CM and David M, 1982. Firing temperature of pottery from predose sensitization of TL. *PACT* 6: 460-467.

The Centre for East Asian Archaeology Studies of Shandong University, 2008. The trial-excavation report of Daxinzhuang site in Jinan City Shandong Province in the autumn of 1984. *Dongfang Kaogu (East Asia Archaeology)* 4, 288-530 (in Chinese).

Watson IA and Aikten MJ, 1985. Firing temperature analysis using the 110°C TL peak of quartz. *Nuclear Tracks and Radiation Measurements* 10(4-6): 517-520, DOI 10.1016/0735-245X(85)90052-3.