Pilot Study on the Lipid Residues in the Ceramic Core of Lost-wax Process

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Abstract： This paper aims to demonstrate the potential of identifying ancient lost-wax process by the means of lipid residue analysis. Ceramic cores from the experimental casting are subjected to examination in order to investigate the absorption behavior and chemical changes of beeswax during the process. The results showed that a considerable amount of wax was absorbed by the ceramic core and underwent various chemical changes under the high temperature condition during the heating and pouring processes. It is revealed that characteristic bio-makers of beeswax such as 14- and 15-hydroxypalmitic acids can sustain a low temperature heating (< 100℃) while certain components including different acids and aldehydes retained when the hearing temperature ranges from 100 to 300℃. There are no lipids components can be detected when the hearing temperature exceeded 400℃. It is demonstrated that the adsorbed organic residues in the casting core can provide empirical evidence for the identification of lost-wax casting under certain circumstances.

Keywords: Lost-wax process; Beeswax; Experimental casting; Lipid residues; GC-MS

1. Introduction

The lost-wax process, also known as *cire-perdue* is a method of metal casting in which the mould was created by means of a wax model. The good workability of beeswax in both solid and liquid form makes this method an efficient solution for casting intricate shapes (Sopcak, 1986). Archaeological evidence revealed that the invention of the lost-wax process can be traced back to over 6000 years ago (Thoury, et al., 2016) , and it has been widely practiced by metalworkers of many ancient civilizations since the 3rd millennium BCE (Hunt, 1980, Davey, 2006). One possible exception could be Bronze Age China given the long dominated tradition of piece mold casting (Bagley, 1987: 15-54). Although it has been generally accepted that the lost-

wax process was already in use from the Spring and Autumn period (8th–5th centuries BCE) (Hua and Jia, 1983, Tan, 1994, Peng, 2020), this view is not without controversy. Recently, some scholars claimed that the bronzes previously believed to be made by the lost-wax process, such as the *Zun* and *Pan* set unearthed from the tomb of Marquis Yi of Zeng (Hua and Guo, 1979), were actually cast in piece-molds (Zhou, et al., 2006, Dong, et al., 2008). This sparked a heated debate on whether the lost-wax process existed in Bronze Age China which continues to this day. One fundamental issue behind the debate is the lack of conclusive criteria for identifying a lost-wax cast artefact, as the same information retrieved by visual and structural inspection can often be explained following various technical logic including piece mold casting (for detailed review and comments of the debate see: Zhang, 2007, Strahan, 2019, Yang, 2021).

Notwithstanding numerous variants, the essential characteristic of the lost-wax process is the introduction of a wax model during fabrication of the mold assemblage. A core within the model would be necessary if one seeks to cast a hollow object (Sopcak, 1986: 4-6). In ancient times, the most accessible material for the model would have been the beeswax, while both the inner core and outer mold were commonly made of clay (e.g. Hunt, 1980, Noble, 1975, Mattusch, 1997: 66-70). Prior to pouring, the wax model needed to melted and drain out to create the cavity that was to be filled by the molten metal. Then, there is a stage that the surfaces of the mold and core were immersed in the molten wax allowing them to absorb some wax due to their porous nature. After pouring and cooling, the mold is broken to retrieve the metal object but sometimes the core may have been left inside the finished object permanently. It is theoretically possible that the absorbed wax would remain in the ceramic core which can be used as a powerful indictor for the identification of the lost-wax process.

Although previous studies have already indicated that beeswax is rather stable and can be chemically identified with lipid residues analyses even after thousands of years of burial (e.g. Heron, et al., 1994, Bernardini, et al., 2012, Roffet-Salque, et al., 2015), little is known about the effect of high temperature processes on it, such as the roasting and pouring that is encountered during the operation of the lost-wax casting. In order to fulfill this lacuna and to testify the aforementioned hypothesis, a series of experiments involving the lost-wax casting were carried out and the ceramic cores were examined following the well-established protocols of lipid residues analyses (Evershed, et al., 2001, Harper, et al., 2017). The main questions to be addressed in this paper are whether molten wax was absorbed by the core during the process and to what

circumstance can its residues be detected and assigned to a beeswax origin.

2. Experiment and analytical methods

2.1 Experiment and samples

A simplified procedure of direct lost-wax casting involves the following steps and was adopted for this research (Feinberg, 1983: 6-10):

- A cylinder clay core (about 5 cm long and 2 cm in diameter) is shaped and dried at room temperature.
- Beeswax sheets (about 2 mm thick) were heated soft and layered on the clay core to create a wax model; iron nails used as chaplets were stuck through the wax layer into the core with their heads left exposed.
- Fine clay plaster was used to cover the model to form an inner layer of the mold (about 5 mm thick), and successive layers of coarse clay (about 5 mm thick) are applied to complete the mould. The wax model is almost totally covered by the clay shell but the sprue and riser vent are left open.
- The completed mold is dried at room temperature for several days and the wax is melted and drained out in a drying cabinet at a temperature of 60 ℃.
- The mold is then roasted in a muffle furnace. To investigate the effect of temperature on beeswax residues, 2 parallel batches of molds (6 of each batch) are roasted at a temperature of 100, 200, 300, 400, 500 and 600℃ respectively. The heating rate was set as 5℃ per hour and the oven was kept at the target temperature for 1 hour.
- One mold from each batch was subjected to casting and the other was kept as roasted for comparison in order to investigate the effect of molten metal during the pouring step. An alloy of 85% copper, 10% tin and 5% lead is used for the cast, it is melted in a muffle at 1200℃ before pouring.
- After cooling at room temperature, the mold is broken and the bronze cylinder with a ceramic core inside is retrieved.

Figure 1 Procedure used for the direct lost-wax casting in this experiment

(a) melting beeswax (b) Applying the beeswax sheets to the clay core (c) drying the cast moulds (d) draining the wax (e) Melting the metal (f) Pouring (g) cutting the cast (h) final sample

The bronze cylinder is then cut at one end to expose the trapped ceramic cores. Powder of the ceramic cores and the as heated cores were taken with a handheld drill for residue analysis. In total, 12 ceramic cores were analysed in this study. Beeswax and the clay were also analyzed for comparison and the data are shown in Supplementary Materials S1.

2.2 Lipid residue analysis

Approximately 2g of powder was taken from the ceramic core of the experimental molds using a Dremel drill. It was then weighed and transferred to a clean glass tube, and n-tritetradecane (10μL of a 1mg mL^{-1}) was added as internal standard. The direct acidified methanol extractions followed established methods (Correa-Ascencio and Evershed, 2014) . The samples (~ 1g) were extracted by ultrasonication in 4mL of methanol for 15min at room temperature. The solution was heated at 70℃ for 4h after adding 800 μL of H_2SO_4, centrifuged at 3000 rpm for 5 min. The liquid extract was transferred to a clean tube by pipetting. Next, 2mL of hexane was added, and the supernatant (hexane layer) was separated and transferred into another clean tube, and this step was repeated twice. The hexane extracts were then dried under a gentle nitrogen stream and transferred into a vial after re-dissolving in 100 μL of hexane, with the addition of 10μL n-tetratriacontane (1mg mL^{-1}) as internal standard. Finally, to the aliquots were added 25μL N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA containing 1% trimethylsilyl chloride at 70℃ for 1h) for derivatization, before GC-

MS analyses. Blank samples were added to each group for detection of contamination.

GC-MS analysis was performed using a Shimadzu GC-MS-QP2010plus. The MS was operated in electron ionization (EI) mode at 70 eV with a GC interface temperature of 300℃ and a source temperature of 200℃. The emission current was 150 mA and the qualitative analysis was conducted under full-scan acquisition mode within m/z 50 – 800 range. Analytes were separated using a Shimadazu SH-Rxi-5Sil capillary column of 30m×0.25mm with a film thickness of 0.1 μm. Helium was used as the carrier gas. 1μL of sample was injected in a split mode (10:1). The oven temperature program was conducted as follows: initial temperature 50℃ for 2 min; ramped at 10℃ min^{-1} to 300℃, and then maintained for 10min. Compound identification were based on their respective retention time, mass spectra and comparisons with the NIST14 and NIST14s Mass Spectrum Library.

In this study, the total lipid concentration extracted from each sample was calculated by area normalization, by using the C_{36} internal standard as the reference concentration.

3. Results and discussion

The total concentrations and components of the recovered lipids from the 12 analyzed core samples are shown in Table 1 and Fig. 2. The total ion chromatograms and component identified for each sample are reported respectively in Supplementary Materials S2. Although lipids residues in all samples were detectable with the GC-MS, they vary considerably in terms of both composition and concentration. As one can imagine, with t increased temperature, the concentration of the residual lipids decreased significantly. The heating during the pouring process further reduced the content of the lipid substances. It is important to note that when the heating temperature is higher than 400℃, the lipid residue contents in the cores become extremely low, even lower than that in the raw clay (4.37μg/g). This finding indicates that the absorbed wax was almost completely incinerated during the heating process.

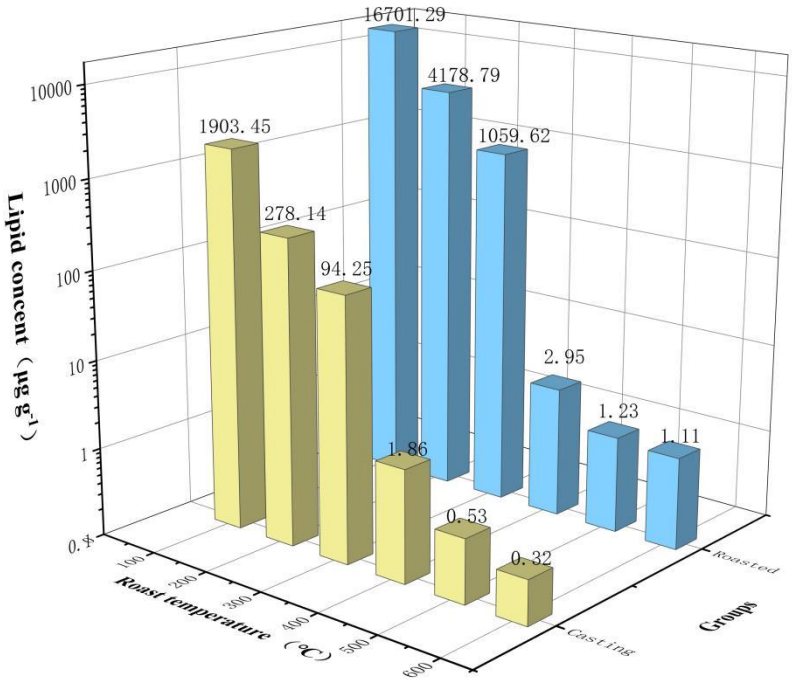

Figure 2 Bar graph of the total lipid contents of clay cores formed under different conditions

3.1 Lipid residues in the heated cores

Sample BS01 contained the highest residual lipid content (16701.29 μg/g). The lipids consisted of a series of saturated fatty acids (even-numbered $C_{16:0–30:0}$), saturated fatty alcohols (even-numbered $C_{22–30}$), and alkanes (odd-numbered $C_{21–33}$), as well as 15-hydroxypalmitic acid, 14-hydroxypalmitic acid, 16-hydroxypalmitic acid, and unsaturated fatty acids ($C_{16:1}$, $C_{18:1}$, $C_{20:1}$, and $C_{22:1}$). Studies have shown that natural beeswax is mainly composed of esters (about 67%) (Tulloch, 1980), hydrocarbons (about 14%), saturated fatty acids (about 16%), and saturated fatty alcohols (about 1%) (Tulloch, 1971, Jiménez, et al., 2004). During the extraction of lipids by the direct acidification of methanol, the esters were hydrolysed to acids and alcohols that were involved in esterification (Correa-Ascencio and Evershed, 2014). In addition, during high-temperature heating, the original components of the beeswax were cleaved or degraded due to the high temperatures. Most of the C_{16} and C_{18} saturated fatty acids, hydroxy acids, and unsaturated fatty acids detected in sample BS01 resulted from the hydrolysis of wax esters. In particular, 14-hydroxypalmitic acid and 15-hydroxypalmitic acid, both of which were the original components of the beeswax, were characteristic markers of the beeswax (Tulloch, 1971, Aichholz and Lorbeer, 1999). The detected fatty alcohols included not only alcohols that were generated from the hydrolysis of wax esters, but also free fatty alcohols that originally existed in the beeswax, while the detected alkanes were the original components of the beeswax. A

large amount of beeswax was adsorbed in the clay core during the lost-wax process, while the components of the beeswax remained largely unchanged after heating at 100°C (Figure 3a).

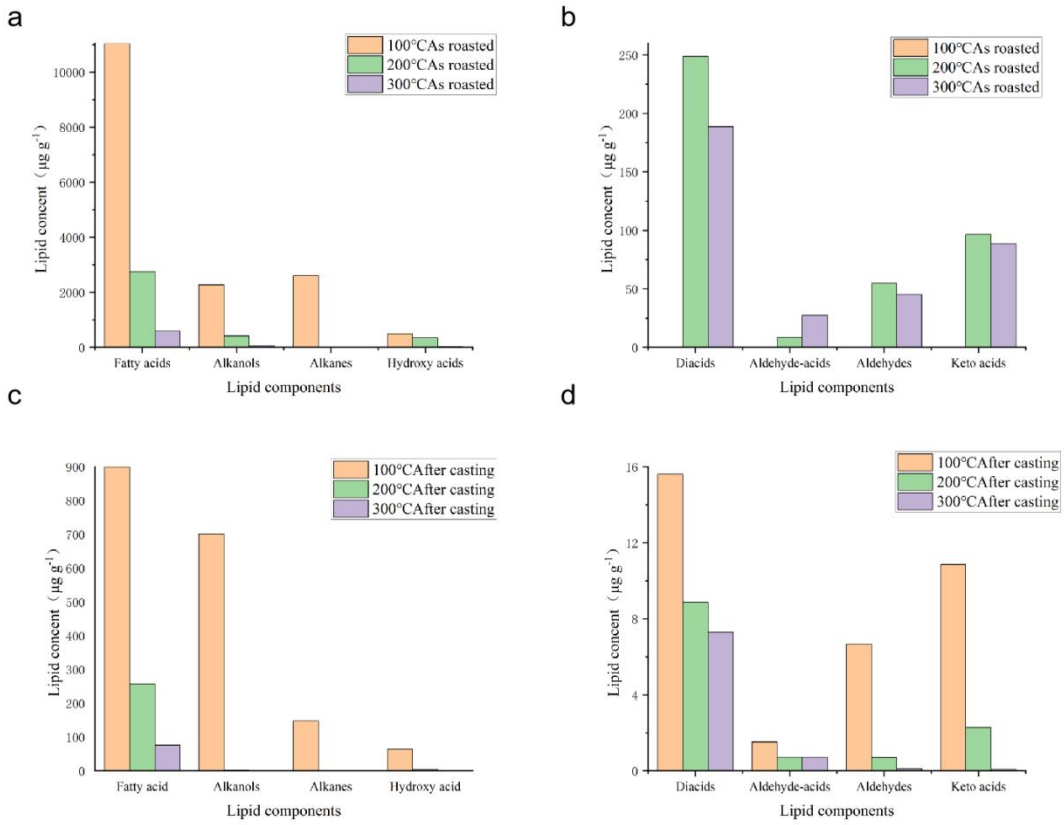

Figure 3 Bar graphs of the main components of lipid residues in clay cores that were heated (a and b) vs. cast (c and d)

Compared with sample BS01, the total lipid contents of samples BS02 and BS03 were significantly lower (4178.79 and 1059.62 μg/g, respectively), with significant changes in the lipid composition. Specifically, the relative content of long-chain even-numbered fatty acids and fatty alcohols was reduced, while these components were replaced to some extent by new consecutive-numbered $C_{7:0–15:0}$ fatty acids, odd-numbered $C_{16:0–30:0}$ fatty acids, consecutive-numbered $C_{8–23}$ fatty acids, odd-numbered $C_{24–30}$ fatty alcohols, and some acid derivatives (diacids, aldehydes, aldehyde-acids, and keto acids). Monounsaturated fatty acids were detected in small amounts as other carbon-numbered unsaturated fatty acids and 22-hydroxydocosanoic acid, in addition to the originally abundant components $C_{16:1}$ and $C_{18:1}$. Meanwhile, the original alkane components in beeswax disappeared completely (Figures 3a and 3b).

Because the ignition point of natural beeswax is 204.4°C (Antony, et al., 2017) and due to the error in the temperature control of the muffle furnace used in the experiment, it was possible that the temperature inside the muffle furnace reached the ignition point during the heating process, even though the heating temperature was set

to 200°C. This suggested that the decrease in the total lipid contents of BS02 and BS03 may have been mainly caused by the combustion of beeswax during the roasting process.. Meanwhile, the residual beeswax components degraded in the presence of oxygen under proper temperatures to form more structurally stable compounds. The carbon–carbon single bonds of long-chain fatty acids and fatty alcohols may have been broken to form short-chain acids and short-chain alcohols (Giese, 1986, Brown and Roger, 1980). Unsaturated fatty acids, however, may have generated diacids due to double bond breakage or monohydroxy acids due to the hydration of double bonds (Regert, et al., 1998, Evershed, 2010). The appearance of some fatty acid derivatives, such as aldehydes and aldehyde-acids, was associated with the oxidation of alcohols (Patai and Zabicky, 1970) or acids under high temperatures (Cao, et al., 2013, Ke, et al., 2019). Sublimation under high temperatures was the main reason for the disappearance of alkanes (Regert, et al., 2001, Ribechini, et al., 2015). It is noteworthy that the characteristic markers of beeswax, such as 14-hydroxypalmitic acid and 15-hydroxypalmitic acid, were still detectable, although their content had become low.

3.2 Lipid residues in the cores after casting

The analysis showed that the contact with the high-temperature liquid metal during the casting process had a significant effect on the beeswax residues in the clay cores. First, under normal atmospheric conditions, high-temperature liquid metal caused the organic material in the clay cores to burn violently. The combustion reaction consumed a large amount of adsorbed beeswax and its decomposition products in the clay cores, resulting in significant reductions in the total lipid contents of the cast clay cores. As shown in Table 1 and Figure 2, the total lipid contents of the cast clay cores were usually one order of magnitude lower than those of the cores that were roasted only.

In addition, the liquid metal also led to variations in the components of adsorption residues. As mentioned earlier in this paper, the lipid components in sample BS01—the sample that was roasted at 100°C—remained essentially the same as that of beeswax, but the analytical results of sample JZ01—a sample that underwent casting—revealed significant differences in the lipid components relative to that of beeswax. For sample JZ01, the identifiable components mainly included saturated fatty acids ($C_{7:0\text{-}27:0}$ and $C_{30:0}$), saturated fatty alcohols ($C_{10\text{-}30}$, C_{32}, and C_{34}), alkanes (odd-numbered $C_{23\text{-}33}$), hydroxy fatty acids (14-hydroxypalmitic acid, 15-hydroxypalmitic acid, 16-hydroxypalmitic acid, 2-hydroxy-octadecanoic acid, 9,10-dihydroxy-octadecanoic acid, and 2-hydroxy-tricosanoic acid), unsaturated fatty acids ($C_{14:1}$, $C_{16:1}$, $C_{18:1}$, $C_{20:1}$, $C_{22:1}$, $C_{24:1}$), as well as other acid derivatives, including diacids ($C_{7\text{-}13}$, C_{16}, C_{18}, and C_{20}), aldehyde-acids (C_5, C_7, and C_8), aldehydes (C_5, C_7, C_8, and C_{11}), and keto acids (C_{18}). In particular, the appearance of short-chain fatty acids, odd-numbered fatty acids, short-chain fatty alcohols, odd-numbered fatty alcohols, other carbon-numbered hydroxy

fatty acids and unsaturated fatty acids, and some fatty acid derivatives (diacids, aldehyde-acids, aldehydes, and keto-acids) was associated with changes in the beeswax components at high temperatures (see Figures 3c, 3d, and 4a).

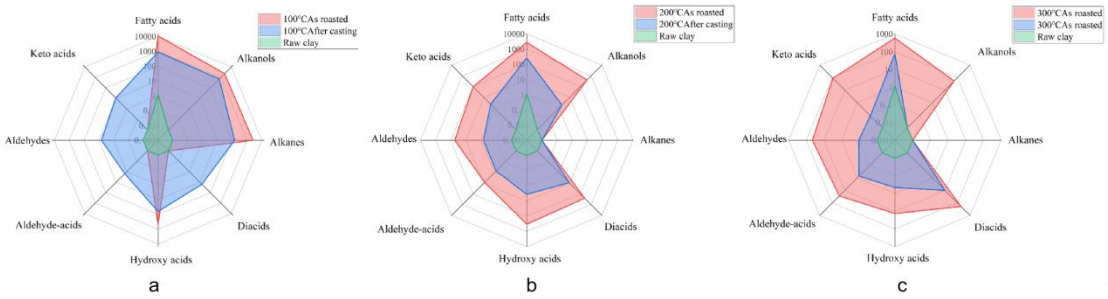

Figure 4 Radar chart showing the compositional characteristics of the adsorbed residues for clay cores that were in different casting states with a roast temperature of (a) 100°C, (b) 200°C, and (c) 300°C

Although the total lipid contents of samples JZ02 and JZ03 were very low (278.14 and 94.25 μg/g, respectively; Table 1, Figure 2), they were still significantly higher than that of the clay raw material and met the general requirements for archaeological residue analysis of the total lipid content (>5 μg/g) (Evershed, et al., 2008, Evershed, et al., 1997) . In terms of the composition of identifiable components, the main components of adsorption residues in the above two samples were in high agreement with those in the corresponding roasted samples (i.e., samples BS02 and BS03), except for the fatty acids, which were significantly lower in content for JZ02 and JZ03. As shown in Figures 4b and 4c, the alkanes in raw beeswax had been completely burned out or volatilized, leaving heat-generated derivatives (i.e., short-chain saturated fatty acids and diacids) as the main components. As a result, 14-hydroxypalmitic acid and 15-hydroxypalmitic acid, which are characteristic markers of beeswax, could no longer be detected in JZ02 and JZ03. However, the fact that the total lipid contents were significantly higher in JZ02 and JZ03 than in the clay raw materials, along with the compositional characteristics of the fatty acids, diacids, hydroxy acids, and aldehyde-acids, still provided an important basis for determining the original ingredient of the residue (i.e., beeswax).

4. Conclusions

Compared with the adsorbed residues in pottery, little is currently known about the high-temperature behaviours of natural oils and fats such as beeswax in the field of archaeological sciences. In this research, we carried out an experimental casting to investigate the adsorption behaviour and residue characteristics of beeswax in clay cores during lost-wax casting. The results showed that a considerable amount of liquid wax was absorbed by the porous ceramic core during the draining out of wax materials. During subsequent mould heating (which may or may not have been performed) and

casting processes, the adsorbed wax underwent various chemical changes under high temperatures. The changes included the combustion of beeswax, sublimation of alkanes, breakage of the carbon chains of unsaturated acids, breakage of the carbon chains of long-chain saturated fatty acids and long-chain saturated fatty alcohols, and oxidation of fatty acids.

Under the experimental conditions of this study, when the heating temperature was low (<100°C), the lipid residues in the cast clay cores were abundant and retained the characteristic markers of beeswax, such as 14- and 15-hydroxypalmitic acids. When the heating temperature was higher than 100°C but lower than 300°C, it was still possible to ascertain that beeswax had been adsorbed in the clay cores by taking into account their relatively high lipid contents along with the characteristics of the main components (i.e., fatty acids, diacids, hydroxy acids, aldehyde-acids, aldehydes, and keto acids). When the heating temperature exceeded 400°C, the lipids adsorbed in the clay cores were nearly entirely depleted, and their contents were not detectable by residue analysis. These results confirmed that adsorbed organic residues in ceramic cores formed under certain circumstances can provide empirical evidence of lost-wax casting, which laid the foundation for the further research.

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Table 1 Total lipid concentrations（μg g^{-1}）and lipid components recovered from 12 simulated cores

Conditions	Samples	Roast Temperature	Lipid components								Lipid content（μg g^{-1}）
			Fatty acids	n-alkanols	n-alkanes	Hydroxy acids	Diacids	Aldehyde-acids	Aldehydes	Keto acids	
As roasted	BS01	100℃	√	√	√	√					16701.29
	BS02	200℃	√	√		√	√	√	√	√	4178.79
	BS03	300℃	√	√		√	√	√	√	√	1059.62
	BS04	400℃	√				√				2.95
	BS05	500℃	√				√				1.23
	BS06	600℃	√								1.11
After casting	JZ01	100℃	√	√	√	√	√	√	√	√	1903.45
	JZ02	200℃	√	√		√	√	√	√	√	278.14
	JZ03	300℃	√			√	√	√	√	√	94.25
	JZ04	400℃	√			√					1.86
	JZ05	500℃	√								0.53
	JZ06	600℃	√								0.32

（BS=as heated samples, JZ=cast samples）