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An analysis of the chemical composition, performance and structure of China Yixing Zisha pottery from 1573 A.D. to 1911 A.D.

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Abstract

Yixing Zisha pottery is one of the most representative and influential traditional tea sets in ancient and even contemporary China. Chemical and phase composition, microstructure and performance of Yixing Zisha pottery samples from the late Ming Dynasty to the late Qing Dynasty (1573 A.D.–1911 A.D.) unearthed for the first time in the Shushan Mountain Zisha pottery kiln sites in the western and southern hills of Shushan Mountain, Dingshu Town, Yixing City, China, were systematically analyzed. The chemical composition variations of Yixing Zisha pottery of the above-mentioned periods were studied. Porous structure of Yixing Zisha pottery body was discovered and the relationships among the unique performance of Yixing Zisha pottery, its raw material and the special technological process were discussed.

Keywords: Zisha pottery; Chemical composition; Micro structure; Physical performance

1. Introduction

Yixing Zisha pottery of Jiangsu Province in China, as it is one of the world's ancient civilization countries, is a kind of important craft with unique features among the great variety of Chinese pottery. Zisha tea pots, known as the most appropriate tea sets in China [1], are not only works of art but also highly popular and utilitarian drinking vessels. The technological process of Yixing Zisha pottery has also been listed as one of the first national intangible cultural heritages of China [2]. Although scholars have paid great attention to Yixing Zisha pottery, their research has mainly been devoted to its humanistic and artistic values—such as appreciation of the color and the shapes of the vessels [3–7], but little attention has been given to the study of its technology [8,9], which is not conducive to the full exploration and comprehensive preservation of the cultural heritage of human beings.

Since July 2007, Shushan Mountain Zisha pottery kiln sites located in the western and southern hills of Shushan Mountain, Dingshu Town, Yixing City have been excavated by The Nanjing Museum of China for the first time. Abundant Zisha pottery samples of five periods dating from the late Ming Dyansty to the late Qing Dynasty (1573 A.D.–1911 A.D.) were unearthed. These unearthed vessels, which are numerous in kinds and with definite time periods, have provided precious first hand information for the in-depth study of Yixing Zisha pottery. With the great support from the Nanjing Museum, systematic researches on the chemical composition and micro-structure, etc. of Yixing Zisha pottery were carried out. The inherent relationships among performance, chemical composition and micro-structure, raw materials and production techniques are discussed.

2. Samples and experiments

2.1. Samples

With the great support of the Nanjing Museum, 31 representative Zisha pottery samples of the above-mentioned periods (Table 1 and Fig. 1), 3 ordinary pottery samples of Qing Dynasty (not Zisha, tq-1–tq-3) and

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Table 1
Major and minor element concentration of Yixing Zisha pottery samples (%).

Period	No.	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
The Late Ming Dynasty (1573 A.D.–1644 A.D.)	mw-1	0.21	0.57	15.48	76.39	1.59	0.26	0.50	4.00
	mw-2	0.03	0.64	17.91	72.56	1.88	0.77	0.57	4.65
	mw-3	0.23	0.56	19.30	69.95	1.78	0.38	0.63	6.16
	mw-4	0.29	0.45	21.13	68.76	2.14	0.36	0.73	5.14
	mw-5	0.04	0.42	19.05	70.89	1.55	0.29	0.64	6.12
	mw-6	0.04	0.39	19.40	70.37	1.94	0.50	0.57	5.79
	mw-7	0.35	0.68	16.63	73.45	1.89	0.63	0.56	4.82
	mw-8	0.03	0.37	23.09	70.92	2.59	0.25	0.64	1.09
The beginning of Qing Dynasty (1645 A.D.–1722 A.D.)	qc-1	0.42	0.78	17.66	72.43	2.00	0.37	0.56	4.78
	qc-2	0.21	0.73	23.11	66.35	1.78	0.26	0.71	5.83
	qc-3	1.01	1.31	19.13	68.69	2.45	0.52	0.69	5.22
	qc-4	0.70	0.83	21.93	62.13	2.85	0.44	0.71	9.40
	qc-5	1.07	2.37	17.77	66.60	2.95	1.92	0.64	5.68
	qc-6	0.81	1.42	21.54	66.16	2.51	0.71	0.69	5.16
The early Qing Dynasty (1723 A.D.–1796 A.D.)	qza-1	0.54	1.26	22.80	62.34	2.65	0.41	0.72	8.29
	qza-2	0.30	2.01	17.16	65.60	4.80	0.56	0.75	7.81
	qza-3	0.38	1.17	21.20	68.16	1.95	0.31	0.67	5.16
	qza-4	0.50	2.15	18.32	69.00	2.82	0.91	0.63	4.67
	qza-5	0.19	0.59	22.31	66.92	1.44	0.47	0.56	6.50
The mid-Qing Dynasty (1797 A.D.–1840 A.D.)	qzh-1	0.57	1.04	25.75	60.09	2.93	0.32	0.70	7.60
	qzh-2	0.61	8.05	13.48	65.91	3.48	1.38	0.59	5.51
	qzh-3	0.27	1.03	20.39	62.24	2.83	0.46	0.79	10.98
	qzh-4	0.51	1.73	20.55	67.26	2.36	0.71	0.60	5.27
	qzh-5	0.52	1.08	22.44	60.85	2.30	0.77	0.63	10.42
	qzh-6	1.26	2.09	20.34	65.53	2.48	1.03	0.67	5.60
The late Qing Dynasty (1841 A.D.–1911 A.D.)	wqmg-1	0.22	0.52	14.26	75.08	1.48	0.42	0.72	6.31
	wqmg-2	0.03	0.47	18.49	68.33	1.97	0.76	0.58	8.35
	wqmg-3	0.58	1.58	18.83	68.50	2.21	0.46	0.72	6.12
	wqmg-4	0.41	0.64	18.35	69.60	1.52	0.41	0.68	7.40
	wqmg-5	0.32	0.94	19.47	66.11	2.37	0.30	0.62	8.86
	wqmg-6	0.25	0.66	17.14	71.15	1.85	0.32	0.52	7.12

3 samples of the ordinary Jingdezhen white porcelain (bc-1–bc-3) as well as 3 samples of the most common raw materials (Dicaoqing, Jiani, Hongni) of Zisha pottery were collected.

2.2. Experiments

Chemical compositions of the Zisha samples of different periods were analyzed by EAGLE-III Energy Dispersion X-ray Fluorescence Spectrometer of the EDAX Company (Tables 1 and 2).

Phase composition of three Zisha raw materials (Dicaoqing, Jiani, Hongni), one common local ceramic clay and two Zisha pottery samples of the late Ming Dynasty and mid-Qing dynasty were analyzed by D/max 2550V X-ray Diffractometer of the Japanese Rigaku Company (Figs. 2 and 3).

Pores distribution of some Zisha pottery samples were observed and analyzed by JXA-8100 Scanning Electron Microscope of the Japanese Electronics Corporation (Fig. 4), and the porosities were measured by the water boiling method (Table 3).

Thermal expansion curves of some Zisha samples were measured by DIL 402C Thermal Dilatometer of the German NETZSCH Instrument Company and the firing temperature of these samples were estimated [10] (Table 3).

Thermal conductivity of samples of different materials were tested by TPS 1500 Thermal Conductivity Analyzer of Sweden Hot Disk Company (Table 4).

Bending strength of samples of different materials was measured by DP-SGW Bending Strength Analyzer of Xiangtan Instrument Limited Company, China (Table 4).

3. Analysis and discussion

3.1. Characteristics of chemical composition

The analysis has shown some chemical composition variation characteristics of Zisha samples of the above-mentioned five periods, which can provide an important basis for the dating study. Generally speaking, the Fe_2O_3 content in these Zisha samples increases over time, ranging from 4.72% to 7.36% while the ratio of SiO_2/Al_2O_3 contained, decreases first and then increases, that is, it

Fig. 1. Samples of the Zisha pottery shards of different periods unearthed in the Shushan Mountain kiln sites of Yixing, China, Note: the background grid 10 mm × 10 mm.

decreases gradually from the late Ming period to the middle Qing period and then increases greatly in the late Qing period. By calculating the mole number of SiO_2, Al_2O_3, R_xO_y (other oxides) and their ratios, variation characteristics of the composition and formula of these samples are discovered (Fig. 5). The ratios of SiO_2/Al_2O_3 and R_xO_y/SiO_2 of the samples from the late Qing Dynasty are close to those from the late Ming Dynasty, which are near the upper left-hand part of Fig. 5. That is, the ratio of SiO_2/Al_2O_3 is relatively high while the ratio of R_xO_y/SiO_2 low. The composition of the samples from the early Qing Dynasty is close to that of the mid-Qing Dynasty, which are distributed on the lower right-hand part of Fig. 5. The fluxing oxide content of the samples from the mid-Qing period is relatively high, with the ratio of R_xO_y/SiO_2 reaching approximately 0.12. Generally speaking, except for the samples from the late Qing Dynasty, the ratio of SiO_2/Al_2O_3 of the samples is gradually decreasing from the average of 6.53 in the late Ming Dynasty to that of 5.52 in the mid-Qing Dynasty while the ratio of R_xO_y/SiO_2 is increasing gradually. Although there is an apparent difference in the major and minor element concentrations of the samples of the above-mentioned periods, the trace element concentrations are very similar (Table 2). The reason for the similarity is similar to that of the development of China Jingdezhen ceramic industry [11]. That is, although raw materials and formula of the ceramics are consistent, the content of the major and minor elements (such as SiO_2 and Al_2O_3), will vary due to the different weathering degrees of minerals in different layers of the mine which has been exploited for a long time.

3.2. Characteristics of structure and performance

When using Yixing Zisha tea pots, people realize that they have many excellent utilitarian performances such as slow heat transfer, good insulation, high intensity, delicate appearance and good tea flavor, which are closely related to the selection and processing of its unique traditional raw materials and its firing techniques, etc.

First, the selection of raw materials is unique. Fig. 2 is the XRD diagram of some kinds of common Zisha raw materials (Dicaoqing, Jiani and Hongni) and ordinary local ceramic clay. The mineral composition of the Zisha

Table 2
Trace element concentration of Yixing Zisha pottery samples (μg/g).

Period	No.	P_2O_5	MnO	CuO	ZnO	Rb_2O	SrO	Y_2O_3	ZrO_2
The Late Ming Dynasty (1573 A.D.–1644 A.D.)	mw-1	290	280	10	80	90	60	40	230
	mw-2	220	270	30	50	110	50	40	300
	mw-3	440	160	40	60	100	40	20	270
	mw-4	460	130	60	70	110	90	40	320
	mw-5	340	390	40	60	80	50	30	460
	mw-6	300	200	80	70	100	60	30	240
	mw-7	390	220	60	60	110	70	30	250
	mw-8	220	270	30	50	110	50	40	300
The beginning of Qing Dynasty (1645 A.D.–1722 A.D.)	qc-1	740	1310	90	90	150	160	50	560
	qc-2	400	160	60	50	90	90	40	380
	qc-3	370	380	20	80	110	110	30	340
	qc-4	360	110	40	50	90	50	30	200
	qc-5	1000	840	70	210	110	50	50	410
	qc-6	530	600	90	70	130	140	30	520
The early Qing Dynasty (1723 A.D.–1796 A.D.)	qza-1	410	230	100	60	110	100	30	310
	qza-2	740	160	70	70	100	100	40	320
	qza-3	400	90	0	10	180	40	10	10
	qza-4	1600	670	50	70	140	180	30	340
	qza-5	420	130	90	50	70	90	50	290
The mid-Qing Dynasty (1797 A.D.–1840 A.D.)	qzh-1	310	130	60	80	120	100	40	240
	qzh-2	2590	430	50	130	140	130	40	290
	qzh-3	1140	190	70	110	110	140	40	410
	qzh-4	410	530	50	70	120	120	30	370
	qzh-5	560	300	60	70	60	40	40	460
	qzh-6	1900	300	70	100	130	100	40	380
The late Qing Dynasty (1841 A.D.–1911 A.D.)	wqmg-1	380	240	40	60	90	60	20	310
	wqmg-2	160	330	70	50	90	50	30	400
	wqmg-3	560	320	50	70	80	50	30	380
	wqmg-4	300	160	80	40	90	60	30	240
	wqmg-5	270	320	50	60	120	70	40	260
	wqmg-6	260	180	120	70	100	70	40	420

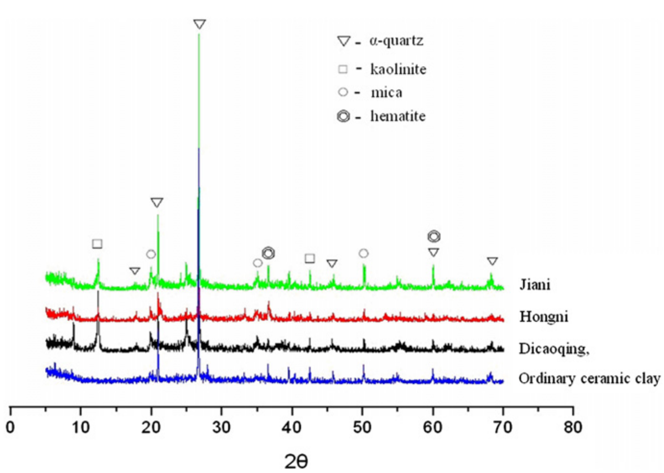

Fig. 2. XRD diagram of Zisha raw material and ordinary ceramic clay.

raw materials consists of mica, kaolinite, α-quartz, and some hematite. Compared with the ordinary ceramic clay, the content of kaolinite in Zisha raw materials is relatively high. The kaolinite crystals in small strips endow Zisha clay with good plasticity while the high content of quartz can reduce the drying shrinkage and firing shrinkage. These are of great significance for the improvement of the strength of the bodies in the process of making Zisha pottery. In addition, the raw material of Yixing Zisha has high Fe_2O_3 content (∼7%) which is equally distributed [2]. FeO decomposed from Fe_2O_3 during high temperature stage of firing process forms low melting point silicate melts combined with SiO_2. It is helpful to promote the sintering degree of body and increase the mechanical strength of products.

Second, the traditional technological process of Yixing Zisha raw materials is much more complicated than that of ordinary potteries and needs more than one processing before it can be used. For example, usually, the freshly exploited Zisha raw materials are as hard as stones which need a few months' natural weathering before they can be ground into powder. Then the powder is sifted and made into raw clay (called "wet clay lump") which in turn should be hammered for about 20 times until the clay (called "ripe clay"), when carved by the knife, gives off luster before it can be adopted to make Zisha pottery. The plasticity index of the refined Zisha clay can reach up to 15.9% with about 8% shrinkage rate, which makes it appropriate for the ‘‘body-beating shaping method’’, a unique handmade shaping method of Yixing Zisha pottery (Fig. 6).

Third, the ‘‘body-beating shaping method’’ is done firstly by continuously beating the clay material with hammer into slices of even thickness. And then the clay slabs are cut and pasted to be a tube whose surface is in turn beat before the form takes shape. The continuous beating can press inward on the crude particles on the surface of the body to make it flat and smooth, endowing Yixing Zisha pottery with unique gradient distribution of pore structure (Fig. 4). It can be found from Fig. 4 that the pores in the outer layer of the Zisha samples are small in size and round in shape, distributed equally in the body whose porosity ranges from 5% to 9%. From the middle layer on, the size of the pores begin to increase gradually and these pores in the shape of small lines scattered in the body with porosity ranging from 9–14%. The chain-like pores in the inner layer are without regular shape, scattered, and inter-crossing in the inner surface of the body, with porosity ranging from 15% to 17%. Therefore, from the outer to the inner layer of the Yixing Zisha pottery, the porosity increases gradually, forming a multi-pore reticulation in vertical gradient distribution.

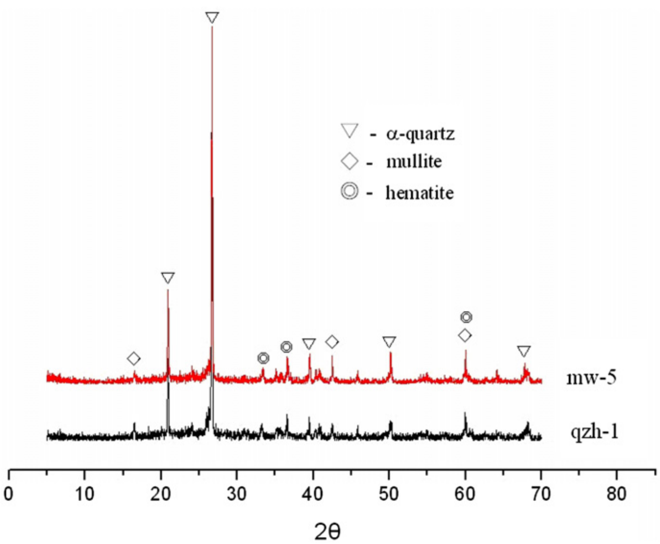

Fig. 3. XRD diagram of typical Zisha samples.

In addition, the firing temperature of Yixing Zisha pottery is higher than that of ordinary Chinese potteries (~800 °C [12]), reaching around 1150 °C (Table 3). Fig. 3 is the XRD diagram of the Zisha samples of two representative periods, namely the late Ming Dynasty (mw-5) and the mid-Qing Dynasty (qzh-1). From Figs. 2 and 3 it can be found that from raw materials to the fired objects, their phase composition has undergone great changes. This is because the kaolinite in Zisha raw materials, after being dehydrated at 450–650 °C, has been decomposed to be metakaolinite, which, with the further rise of temperature, is transformed into Al–Si spinel. Some of Al–Si spinel, at the temperature around 1050 °C, is transformed into primary mullite and formless quartz.

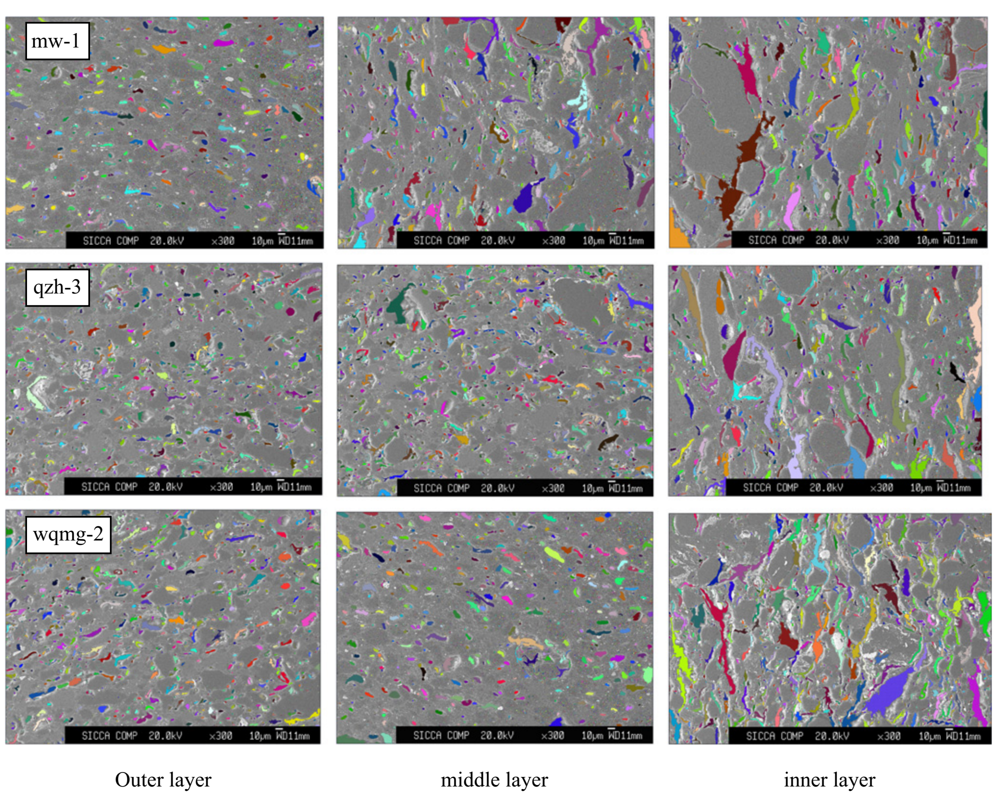

Fig. 4. The distribution of pores in different layers of typical Zisha samples (Note: the porosity of the outer layer is 5–9%, that of the middle layer is 9–14% and that of the inner layer is 15–17%).

Table 3
Firing temperature and average porosity of Zisha pottery samples, ordinary potteries and white porcelains.

Samples	No.	Firing temperature (°C)	Average porosity (%)
Zisha pottery	mw-1	1140	10.81
	mw-5	1120	11.94
	qc-1	1110	12.42
	qc-2	1160	10.46
	qc-3	1150	9.66
	qza-1	1070	13.21
	qzh-1	1130	8.40
	qzh-3	1100	9.23
	wqmg-2	1110	11.03
	wqmg-3	1170	9.36
	wqmg-4	1160	9.95
Ordinary pottery	tq-1	950	18.33
	tq-2	930	17.11
	tq-3	950	17.60
White porcelain	bc-1	1300	2.62
	bc-2	1280	2.46
	bc-3	1280	2.37

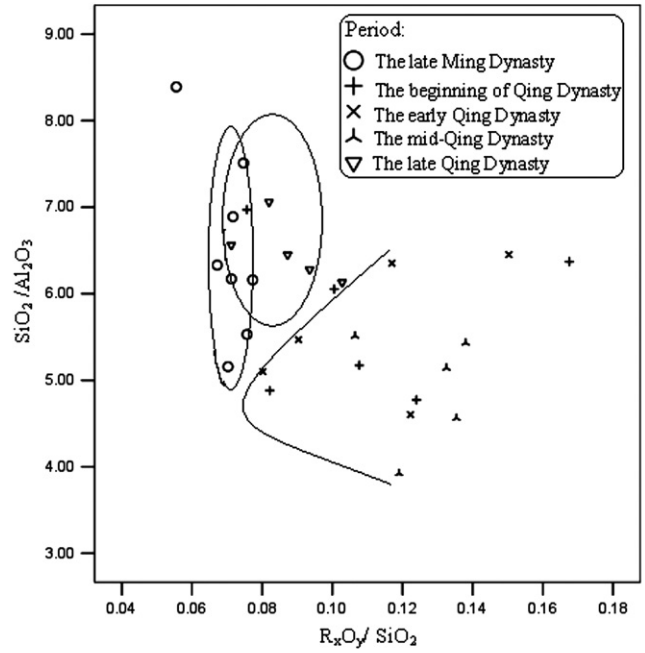

Fig. 5. Scatter diagram of the SiO_2/Al_2O_3 and R_xO_y/ SiO_2 of Zisha samples.

Table 4
Thermal conductivity and bending strength of representative Zisha pottery samples, ordinary potteries and white porcelains.

Samples	No.	Thermal conductivity (KW/M °C)	Bending strength (MPa)
Zisha pottery	mw-1	1.30	38.6
	qzh-3	1.34	47.8
	wqmg-2	1.28	40.5
Ordinary pottery	tq-1	1.18	11.3
	tq-2	1.09	12.5
	tq-3	1.13	12.2
White porcelain	bc-1	1.67	68.4
	bc-2	1.55	54.4
	bc-3	1.59	58.1

When it reaches 1150 °C, some of the mica in the raw material is transformed into glass phase [13]. This makes the phase composition of Yixing Zisha pottery different from that of the ordinary Chinese pottery fired at a lower temperature. The former with low porosity (Table 3) and more compact body can ensure itself with relatively high mechanical strength.

The unique inner pore structure and phase composition of Yixing Zisha pottery has endowed it with excellent performance as tea sets. Table 4 has listed the thermal conductivity and bending strength of Zisha pottery samples, the ordinary pottery and white porcelain samples. It can be found that the thermal conductivity of these three kinds of samples vary basically in inverse proportion to the porosity. The thermal conductivity of the white porcelain is the largest while that of the ordinary pottery the smallest and that of the Zisha pot lies right in between. In ceramic material, the pore is a kind of dispersion phase which hinders the heat transfer and usually can reduce the thermal conductivity of the matrix. The ordinary pottery, due to its high porosity reaching around 18%, has the lowest thermal conductivity and good insulation but loose texture, low mechanical strength and crude appearance. Therefore, it is unsuitable for tea sets. As to white porcelain pot, although with high mechanical strength and delicate appearance, its high thermal conductivity and poor insulation makes it difficult for the extracts of the tea to dissolve fully, affecting, to some extent, the traditional Chinese tea-sipping effect. Yixing Zisha pottery, however, has found a good equilibrium point. Although the porosity of the Yixing Zisha pottery samples reaches around 10%, this value is the average porosity of the whole body. As stated above, the low porosity and compactness of its outer surface helps make the delicate appearance of Zisha pottery while the high porosity of its middle and inner layer endows it with good insulation and sufficient dissolution of the tea extracts, hence the improvement of the effect on the tea [14]. In addition, the inner layer with high porosity can, to a certain degree, absorb and save the organic component leached from the tea. Therefore, after being used for a long time, the pot can produce a unique effect by giving off the fragrance of tea merely with hot water in it. What is worthy of mentioning is that its unique pore distribution and phase composition

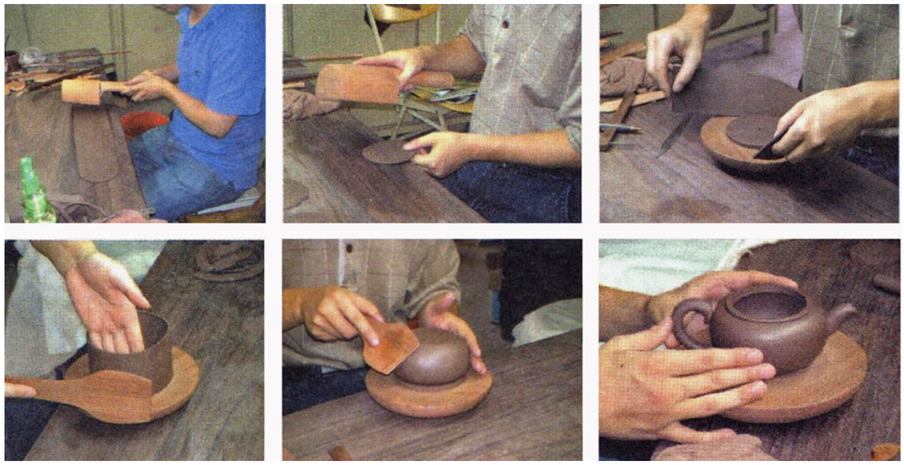

Fig. 6. The traditional shaping method of Yixing Zisha pottery.

can also guarantee a necessary mechanical strength, making a Yixing Zisha pot the most appropriate tea set.

4. Conclusions

(1). The major and minor element concentration characteristics of Yixing Zisha pottery from the late Ming Dynasty to the late Qing Dynasty (1573 A.D.–1911 A.D.) can provide an important basis for the dating study of Zisha pottery, while the similarity of the trace element concentrations has shown that the raw mineral source of Yixing Zisha pottery of the above-mentioned periods is relatively stable.

(2).The selection and delicate processing of raw materials, its unique shaping technique (called the "body-beating shaping method") and its firing temperature far higher than that of ordinary Chinese potteries, not only guarantee the necessary mechanical strength of the vessels, but also contribute to the unique gradient distribution of pore structure of Yixing Zisha pottery. Compact outer surfaces make the delicate appearance of Zisha pottery while the high porosity of its middle and inner layer endows it with good insulation and wonderful traditional Chinese tea-sipping effect, making Zisha pot one of the most appropriate tea sets in China.

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