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The compositions and pore structures of Benshanzhu Zisha ceramic

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Abstract

Yixing Zisha ceramics are popular traditional tea sets with a long history in China but there are seldom studies to explore their compositions and microstructures. In this work, Benshanzhu-Zisha, a typical representation of Zisha from Yixing City of China, is investigated. The XRD results demonstrate that the Benshan Zhu clay is the natural mineral compound, which contains the high hematite content. After sintering, in comparison with pottery and porcelain, Benshanzhu-Zisha has the highest hematite (11.5 wt%) and amorphous phase (71.2 wt%) and the lowest mullite (10.7 wt%). Moreover, there are many dispersed and thin pores in Benshanzhu-Zisha ranging from nanometer to micron, and there are large numbers of hematite particles in the pores. It is the unique pore structures that make Benshanzhu-Zisha be perfect brewing tea vessel, impermeable to water but breathable to gas.

1. Introduction

Yixing Zisha ceramic is the most representative and influential traditional tea sets in ancient and contemporary China, especially for tea brewing [1]. They have passed through a thousand years of history and the technological process of Yixing Zisha ceramic has also been listed as one of the first national intangible cultural heritages of China. Until now, the unique charm of Zisha has attracted the attentions of some scholars. Some reports focus on the artistry and humanity history of Zisha [2–4]. Furthermore, several reports point that the high porosity is the reason of its perfect tea brewing effect [5, 6]. Recently, Dicaoqing-Zisha ceramic is reported by scientifically research [7]. However, Zisha ceramic actually, is a very big family containing many members. Each member has its particular features. It is worth exploring the compositions, microstructures and the relationship of each member for Zisha ceramics.

Yixing Zisha ceramics are made from different Zisha clays. And conventionally, the clays' names are also used to name the corresponding Zisha products. Different raw clays lead to great differences in the properties of the Zisha products. Red clay Zisha is one of the three broad categories of Yixing Zisha, the two others are Purple clay Zisha and Duan clay Zisha [8]. The Zisha clays from Huanglong Mountain mining district, Yixing City, Jiangsu Province, China are collectively called the "Benshan Clay". Zhu clay belongs to Red clay. Its ores are distributed between the Red clay layer or shelf soil and tender clay ore layer, closer to the land surface. Since the Zhu clay is weathered by the infiltration of surface rainwater into the tender clay layer with different degrees, the thickness of Zhu clay ore layer is also different, the thick could be several meters, and the thin could be only a few centimeters. Yield of Red clay is less than Purple clay and Duan clay, further, Zhu clay is a rare class of Red clay. Zhu clay from Huanglong Mountain mine called Benshan Zhu clay, i.e. the material of Benshan-Zhu clay Zisha, labeled as Benshanzhu-Zisha.

In this work, we focus on the compositions and microstructures of Benshanzhu-Zisha. The mechanisms about the formation of the compositions and pore structures of Benshanzhu-Zisha are demonstrated by relating to the minerals of Benshanzhu clay. First, the Benshanzhu clay is the natural mineral compound which contains illite of 24.1 wt%, kaolinite of 15.7 wt%, montmorillonite of 9.2 wt%, hematite of 9.3 wt% and goethite of 10.1 wt%. Second, comparing with porcelain and pottery, the Benshanzhu-Zisha has the highest contents of hematite (11.5 wt%) and amorphous phase (71.2 wt%) due to its low content of Al_2O_3 but extremely high content of Fe_2O_3 of its clay. And the content of mullite in Benshanzhu-Zisha (10.7 wt%) is much lower than porcelain and pottery. What's more, there are many dispersed and thin pores on the surface of Benshanzhu-Zisha, which have a wide pore size distribution ranging from micro to nano scale. Moreover, there are large numbers of hematite particles in the pores. Benshanzhu-Zisha has unique pore structures make the Zisha impermeable to water but breathable to gas, i.e. a perfect tea vessel.

2. Materials And Methods

2.1 Materials

Benshanzhu raw material was obtained from Dingshu town, Yixing city, Jiangsu province, China. The formula porcelain material in this work was purchased from Jingdezhen, China. As far as the pottery, it is an earthen pot was purchased from a commodity market.

2.2 Samples preparation

Before the Benshanzhu raw material becoming green body, it was processed by selecting, grinding sifting, and then aged by natural weathering for a few months. And then the aged materials were processed by continuously beating and crafting to green body. The sintering process of Benshanzhu-Zisha is as follows: Benshanzhu green bodies were dried in a vacuum oven at 80°C for 24 h. Then the dried samples were fired in a Muffle Furnace, they were sintered from room temperature to 300°C with a rate of 3°C/min and held for 30 min, and then the temperature was raised from 300°C to 700°C with a rate of 7°C/min and held for 30 min. Finally, the samples were sintered from 700°C to 1180°C with a rate of 5°C/min and held for 30 min.

The green body of porcelain, cut from the commercial formula porcelain material, was first fired from room temperature to 100°C at a rate of 2°C/min and held for 30 min, then the temperature was increased to 200°C at a rate of 2°C/min and then increased to 300°C at a rate of 2°C/min, both the two temperatures were held for 30 min. After that, the temperature was raised from 300°C to 600°C at a rate of 8°C/min and then raised to 1000°C at the same rate; both of the two temperatures were held for 30 min. Finally, the porcelain sample was fired from 1000°C to 1320°C by 8°C/min and held for 30 minutes.

2.3 Characterization

The crystalline phase composition of samples were tested by using X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) (XRD, D8 Advanced, Brucker). The Infrared Spectroscopy (IR) results were obtained by Fourier transform infrared spectrometer (Nicolet iS50, Thermo Fisher). Thermal analysis of Dicaoqing green body was measured by using TG-DSC simultaneous thermal analyzer (STA449F5, Netzsch) at rate of 5℃/min and air atmosphere. The chemical compositions of samples were characterized by X-ray fluorescence spectrometer (XRF, AXIOSmAX, PANalytical B.V.). The morphologies of samples and the micro analysis were captured by field emission scanning electron microscope (FESEM, SU8010, Hitachi) and the attached energy dispersive spectroscopy (EDS). Pore size distribution and specific surface area were characterized by both mercury porosimetry (Poromaster GT-60, Quantachrome) and nitrogen gas absorption-desorption method (Autosorb-iQ2-MP, Quantachrome).

3. Results And Discussion

The whole body of teapot which is made of Benshanzhu clay has a bright red color and the Benshanzhu raw material is a yellow mineral (Fig. 1). We characterized the mineral phases of green body of Benshanzhu-Zisha by X-ray diffraction. As illustrated in Fig. 2, the main mineral phases of green body of Benshanzhu-Zisha include hematite, goethite, quartz and clay minerals. Besides, there is a small amount of K-feldspar and anorthose. Specifically, the content of each mineral phase is shown in Table 1 (measured by Rietveld refinement). Among those mineral phases, the total contents of clay minerals (montmorillonite + illite + kaolinite) are 49 wt%, illite (24.1 wt%) is significantly higher than other two clay minerals, kaolinite (15.7 wt%) takes the second place, with minimum percentage of montmorillonite (9.2 wt%) in the clay minerals. Moreover, the green body has much amount of hematite (9.3 wt%) and goethite (10.1 wt%).

Table 1
The mineral compositions of the green body of Benshanzhu-Zisha

Mineral phases	Quartz	K-feldspar	Anorthose	Hematite	Goethite	Illite	Kaolinite	Montmorillonite
wt %	29.4	1.1	1.2	9.3	10.1	24.1	15.7	9.2

Figure 3 is the TG-DSC analysis of Benshanzhu-Zisha green body, and corresponding differential results (DTG and DDSC curves). The TG analysis of the Benshanzhu-Zisha green body shows an overall weight loss of 9%. Benshanzhu-Zisha green body has two clear endothermic valleys at about 245°C and 450°C, accompanied by obvious continuous mass loss, which results from the features of illite and montmorillonite [9]. The removal of absorbed water in clay minerals leads to the endothermic valley at 245°C, while the removal of structural hydroxyl groups leads to the endothermic valley at 450°C [10–12]. There is an exothermic peak at 1043°C, which is ascribable to the new formation of crystalline phases during firing [13–15].

Table 2 shows the chemical compositions of Benhsanzhu-Zisha green body, porcelain and pottery. The mass percentage of Al_2O_3 of Benshanzhu-Zisha green body, 19.53 wt%, is less than that of porcelain and pottery. This result should be resulted from its low total mass percentages of clay minerals, which, further, consist of high content of illite but low content of kaolinite. The total contents of alkali metal oxide and alkali earth metal oxides ($K_2O + Na_2O + MgO + CaO$) of Benshanzhu-Zisha green body (3.35 wt%) are also lower than that in porcelain (4.83 wt%) and pottery (7.35 wt%). But it is worth noting that Benshanzhu-Zisha green body has much higher content of Fe_2O_3 than others thanks to the rich hematite and goethite.

Table 2
Chemical compositions of Benhsanzhu-Zisha, porcelain and pottery

wt %	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	TiO_2	P_2O_5	L.O.I
Porcelain	66.50	21.92	0.47	0.12	0.37	0.89	3.45	0.09	0.04	0.08	6.04
Benshanzhu-Zisha	48.16	19.53	18.49	0.70	0.11	0.20	2.34	0.01	0.64	0.20	9.13
Pottery	63.27	26.35	2.27	0.49	2.36	0.78	3.72	0.12	0.32	0.02	0.20

The XRD patterns and quantitative analysis results of the Rietveld refinement for fired porcelain, Benshangzhu-Zisha and pottery are also investigated (Table 3 and Fig. 4). The pottery is comprised of amorphous phase (52.9 wt%), mullite (22.0 wt%), quartz (16.6 wt%), anorthite (7.6 wt%) and few cristobalite (0.5 wt%) and rutile (0.4 wt%). Pottery is usually fired at a low temperature (below 1000°C). Therefore, its reactions during firing are not sufficient. Hence, we mainly compared the chemical compositions and crystalline phases of Benhsanzhu-Zisha with that of porcelain. As shown in Table 3, the content of mullite in Benshanzhu-Zisha (10.7 wt%) is much lower than porcelain (24.7 wt%) and pottery (22.0 wt%), but Benshanzhu-Zisha has the highest contents of hematite (11.5 wt%) and amorphous phase (71.2 wt%) among the three ceramics. The low content of mullite of Benshanzhu-Zisha can be ascribed to the insufficient Al_2O_3. And the significantly high content of hematite and amorphous phase should be contributed to the very rich Fe_2O_3. Although the total contents of alkali metal oxide and alkali earth metal oxides in Benshanzhu-Zisha is lower, it contains much higher Fe_2O_3 than porcelain and pottery, which contributes to the melting of massive SiO_2 and Al_2O_3 and forming large amounts of liquid phase. When firing was ended, the formation of mullite only consumes a few SiO_2 due to the short content of Al_2O_3. Besides, the amount of quartz of Benshanzhu-Zisha is also the lowest one, 6.4 wt%. At last, the rest liquid that contains very rich iron ions will be transformed to (1) the hematite and (2) the amorphous phase.

Table 3
The quantitative analysis results (wt%) of the Rietveld refinement for Benshanzhu-Zisha, porcelain and pottery.

	Quartz	**Mullite**	**Hematite**	**Anorthite**	**Cristobalite**	**Rutile**	**Amorphous**
Porcelain	31.4	24.7	0	0	0	0	43.9
Benshanzhu-Zisha	6.4	10.7	11.5	0	0.2	0	71.2
Pottery	16.6	22.0	0	7.6	0.5	0.4	52.9

As shown in Fig. 5, the microstructures and pore size distributions of pottery, Benshanzhu-Zisha and porcelain were also tested. The microstructure of pottery maintains plenty of large and irregular pores with sharp corners, and the pore size distribution of pottery is mostly concentrated on 1 μm. Benshanzhu-Zisha contains many dispersed and thin pores; it shows a wide pore size distribution ranging from micro to nano scale. The pores of porcelain are large and round in shape. The pores in porcelain mainly focus on around 0.2 μm and dozens of microns, and the distribution is relatively sparse.

Table 4
Porosity characterizations of porcelain, Benshanzhu-Zisha, and pottery.

	Porosity (vol%) by mercury porosimetry	Pore volume (ml/g) bymercury porosimetry	Specific surface area (m^2/g) by mercury porosimetry	Pore volume (ml/g) by BET measurement (10^{-3})	Specific surface area (m^2/g) by BET measurement
porcelain	15.25	0.08	3.08	10.46	7.16
Benshanzhu-Zisha	2.85	0.01	0.65	13.90	8.57
pottery	20.62	0.10	0.98	14.52	10.84

Table 4 shows the porosity characterizations of porcelain, Benshanzhu-Zisha, and pottery. The porosity characterizations are tested via both mercury porosimetry and BET measurement. When measured by mercury porosimetry, the Benshanzhu-Zisha mercury has the lowest porosity, pore volume and specific surface area compared with porcelain and pottery, however there is a large improvement of the data when measured by BET. The pore volume and specific surface area of Benshanzhu-Zisha is still lower than pottery, but higher than porcelain. It is known that the BET measurement depends on the nitrogen absorption and desorption in the pore while the mercury porosimetry depends on the filling of mercury into the pore. Compared with porcelain, it’s difficult for mercury to fill into the thin pores of Benshanzhu-Zisha, while gas filling is not affected. No matter which method is chosen, the pottery shows better pore volume and specific surface area than porcelain and Benshanzhu-Zisha, which could be attributed to its plenty of large pores.

Moreover, more specific microstructures of Benshanzhu-Zisha were investigated. The morphologies of two typical pores could be seen in Figs. 6(a) and 6(b). We analyzed the EDS results of 5 spots of the two typical pores to further discover their features, spots 1–3 for pore 1 in Fig. 6 (a) and spots 4 and 5 for the pore 2 in Fig. 6 (b). The inner wall of pore 1 is smooth without obvious particulate matters. According to the EDS results of spots 1–3, from spot 1 to spot 3, the contents of SiO_2 and Al_2O_3 are increased gradually, while the content of Fe_2O_3 is dramatically decreased. The iron ions mainly concentrate in the pores. Compared with pore 1, there are lots of particulate matters in the pore 2. The EDS result of spot 4 clearly shows the composition of the particulate matter, it is Fe_2O_3. Therefore, these particulate mattes are hematite crystals. When moving outside, the spot 5 beside the pore reveals a falling tendency for the Fe_2O_3 content, while the contents of SiO_2 and Al_2O_3 are increased.

As discussed above, pottery is usually fired at a low temperature. The liquids in pottery were at the early stage when the firing was stopped. Early liquids are dispersed spots and have tendency to flow to the nearby liquid spots. At the same time, pottery possesses good contents of alkali metal oxide and alkali earth metal oxides, which facilitated to formation of liquids. But the firing was early ended due to the low fire temperature, and all reactions were ended abruptly. After crystallizations and amorphization, plenty of large pores are formed at the sites of early liquid and maintain the shapes of early liquids. As for porcelain, it was fired at 1300°C, and has sufficient $K_2O + Na_2O + MgO + CaO$, liquids would flow throughout all over the body [16]. After the complete crystallizations, the residual liquid with low viscosity filled the pores and formed the amorphous phase. A few large pores may be bubbles that retained in liquid. Thereby, the porcelain is dense and pores of porcelain are round and the quantity is much less than that of pottery and Zisha. Benshanzhu-Zisha was fired at a middle temperature (1180°C) compared with pottery and porcelain. At the same time, it has massive liquid during firing due to the very rich Fe_2O_3. The EDS results support to our speculation that Fe_2O_3 plays an important role in formation of liquid since Fe_2O_3 concentrates in pores and the pores are formed at liquid sites after the crystallization and formation of amorphous phase. However, the liquid with such many iron ions should be of high viscosity. It is different from the liquid that consists of rich $K_2O + Na_2O + MgO + CaO$, which are known as their capability of fluxing and reducing viscosity [17]. After the firing was stopped, crystalline and amorphous phase that were generated from liquids could fill, but not completely, those pores from ignition loss because the liquids have viscosity obstacle. Hence, there are still many thin pores survived. In addition, the EDS analysis reveals that iron ions have two places to go: one is to form hematite and the other is to retain in the amorphous phase. Accordingly, the pores of Benshanzhu-Zisha show two typical morphologies: one has smooth inner wall, the other contains many hematite particles in pores. It's obviously that the hematite crystals can narrow the pore and form an uneven inner wall, which is difficult to be filled by mercury but permits the gas passing through. This result is accord with the porosity characters of Benshanzhu-Zisha shown in Table 4, which also account for the good breathability but no water seepage of Zisha ceramics.

4. Conclusions

The Benshanzhu-Zisha ceramic is investigated including the minerals compositions of raw materials, crystalline compositions and pore structures. Benshanzhu-Zisha clay is a natural mineral compound, which consists of illite of 24.1 wt%, kaolinite of 15.7 wt%, montmorillonite of 9.2 wt%, hematite of 9.3 wt% and goethite of 10.1 wt%. Compared with porcelain and pottery, the content of mullite in Benshanzhu-Zisha (10.7 wt%) is much lower than porcelain (24.7 wt%) and pottery (22.0 wt%), but Benshanzhu-Zisha has the highest contents of hematite (11.5 wt%) and amorphous phase (71.2 wt%) among the three ceramics due to its low content of Al_2O_3 but extremely high content of Fe_2O_3 of its clay. Based on the compositions, Benshanzhu-Zisha ceramic is bright red in color. Benshanzhu-Zisha contains many dispersed and thin pores, which have a wide pore size distribution ranging from micro scale to nano scale. Moreover, there are large numbers of hematite particles in the pores. The unique pore structures endow it with the good breathability but no water seepage, which account for its reputation of perfect tea sets.

Declarations

Acknowledgement

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Figures

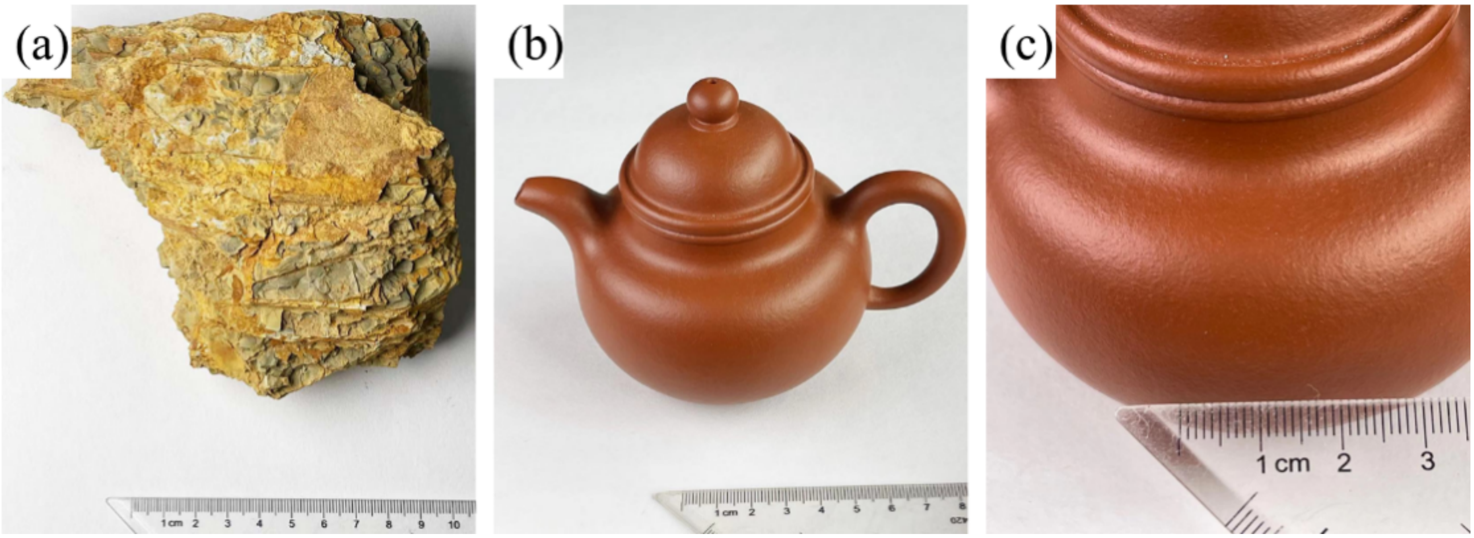

Figure 1

Photograph of (a) Benshanzhu-Zisha raw material, (b) Benshanzhu-Zisha teapot and (c) close-up photograph of surface.

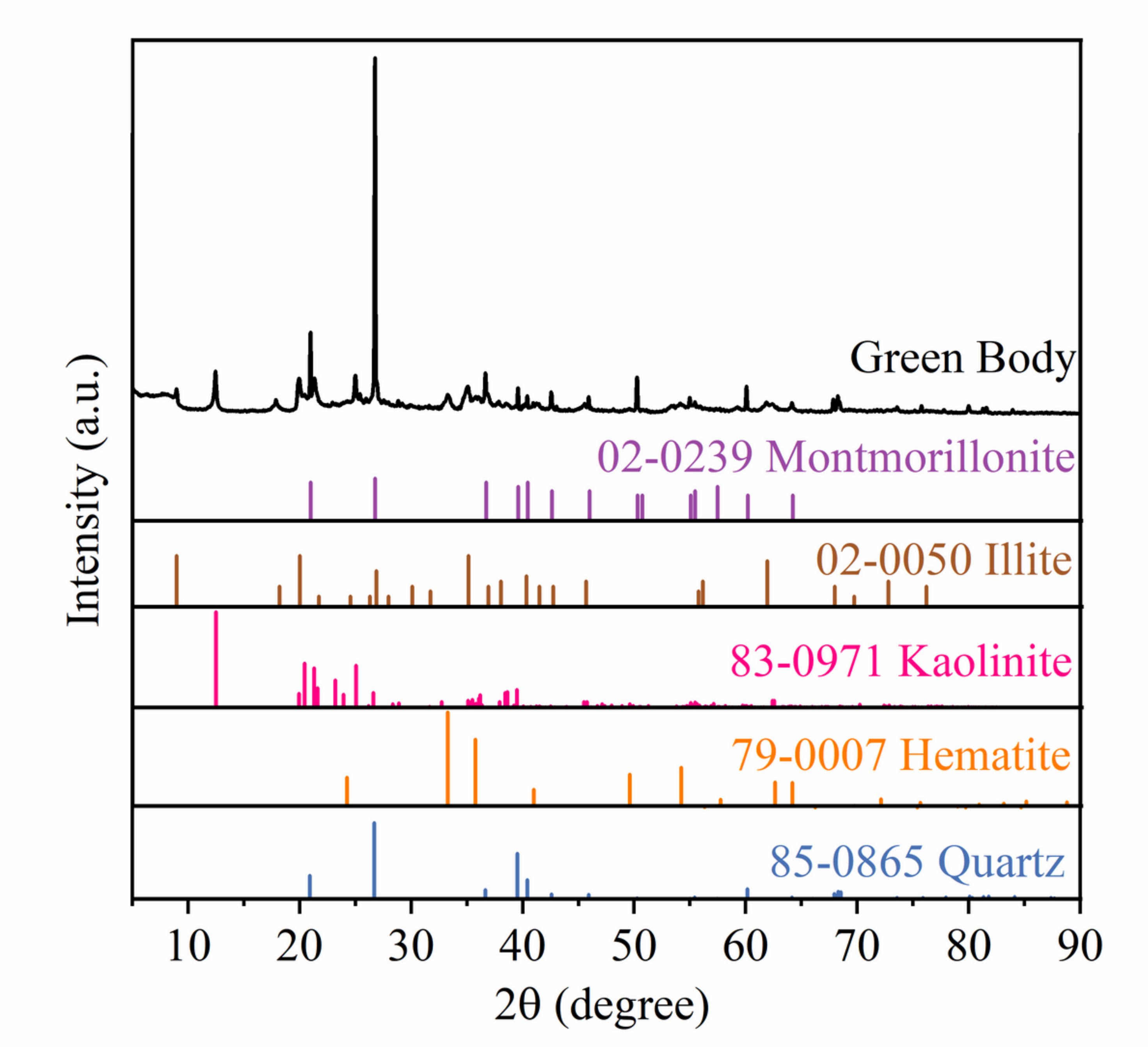

Figure 2

XRD pattern of the green body of Benshanzhu-Zisha.

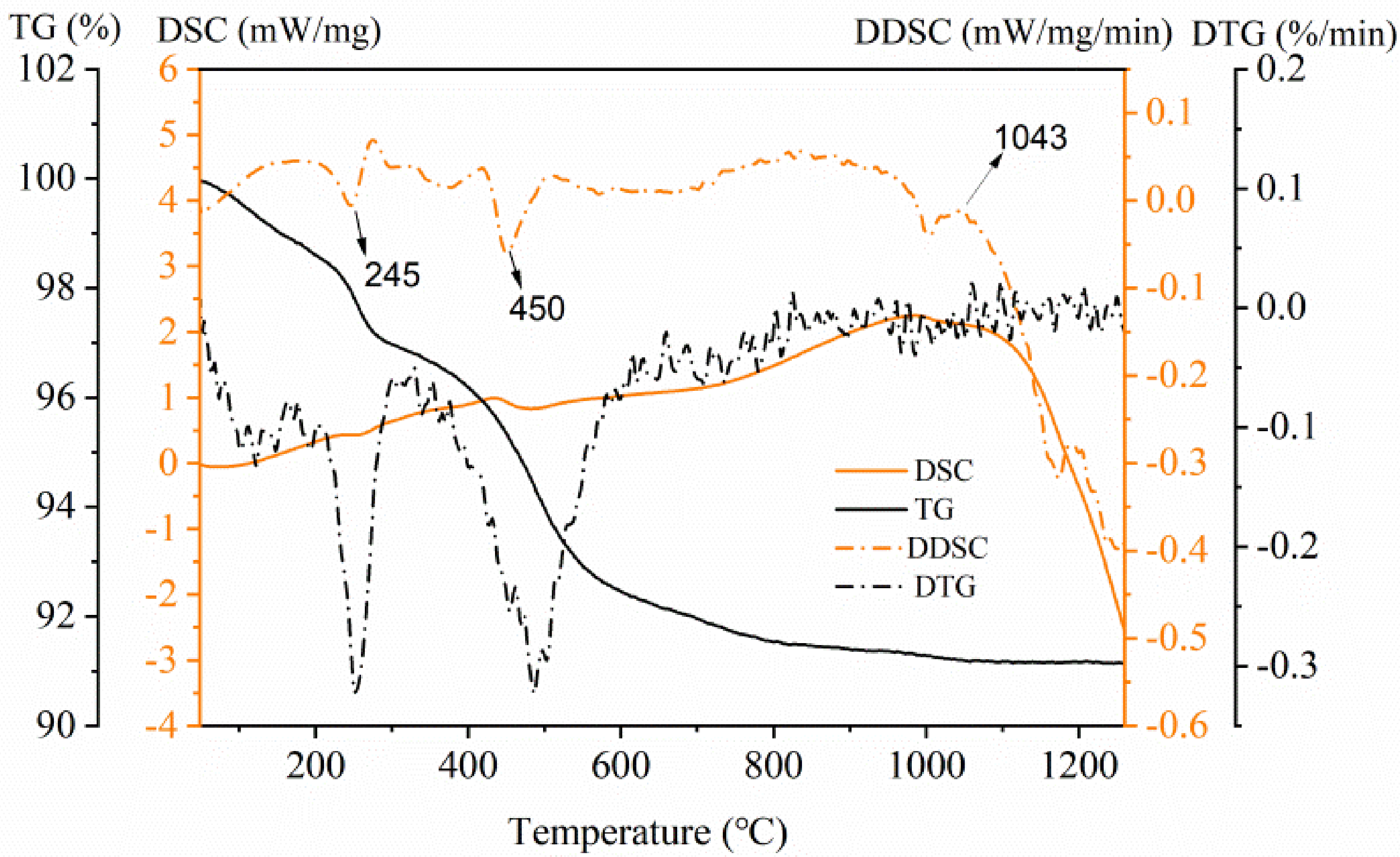

Figure 3

TG-DSC analysis of Benshanzhu-Zisha green body, the DTG and DDSC curves are the corresponding differential results.

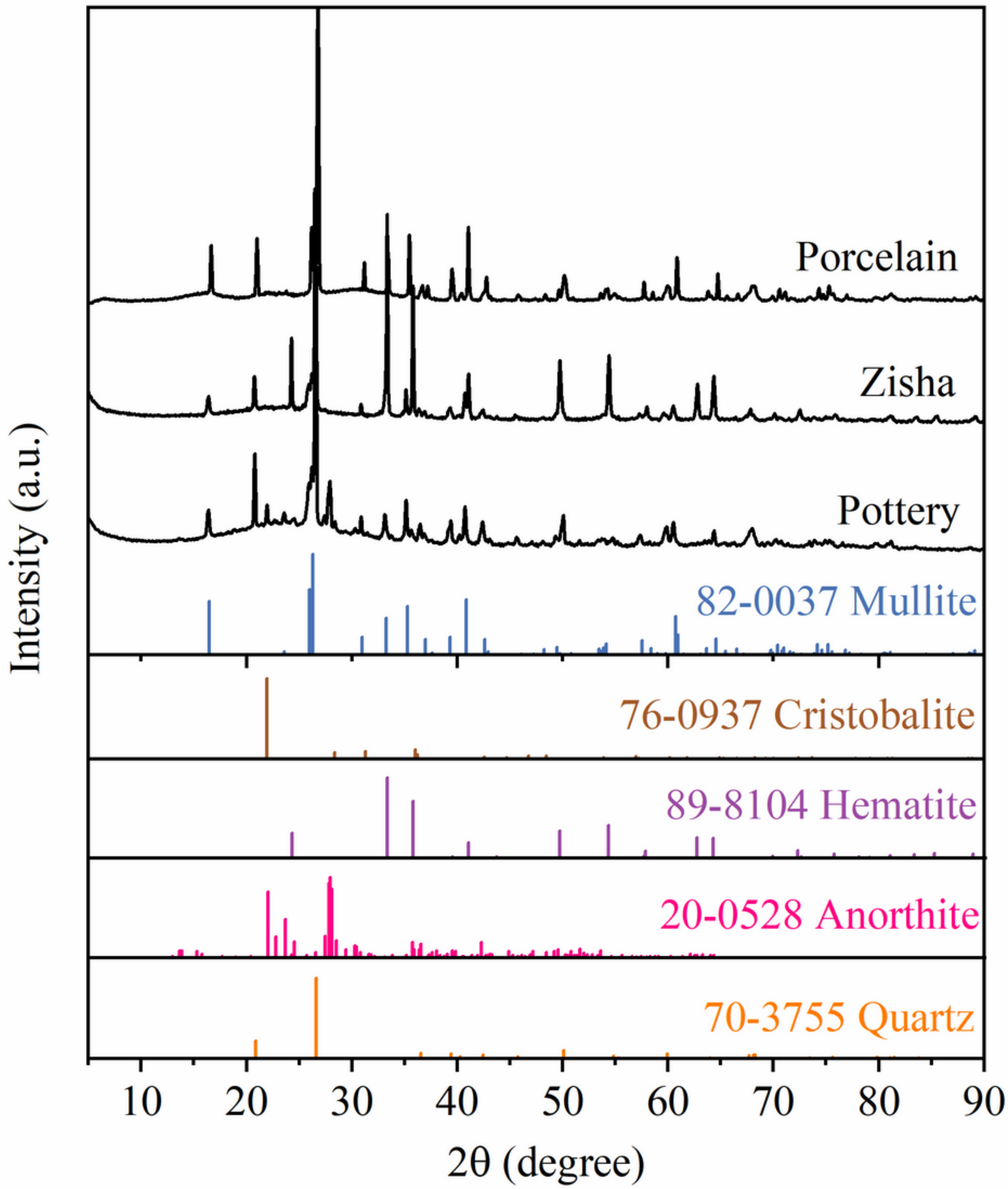

Figure 4

XRD patterns of porcelain, Benshangzhu-Zisha and pottery

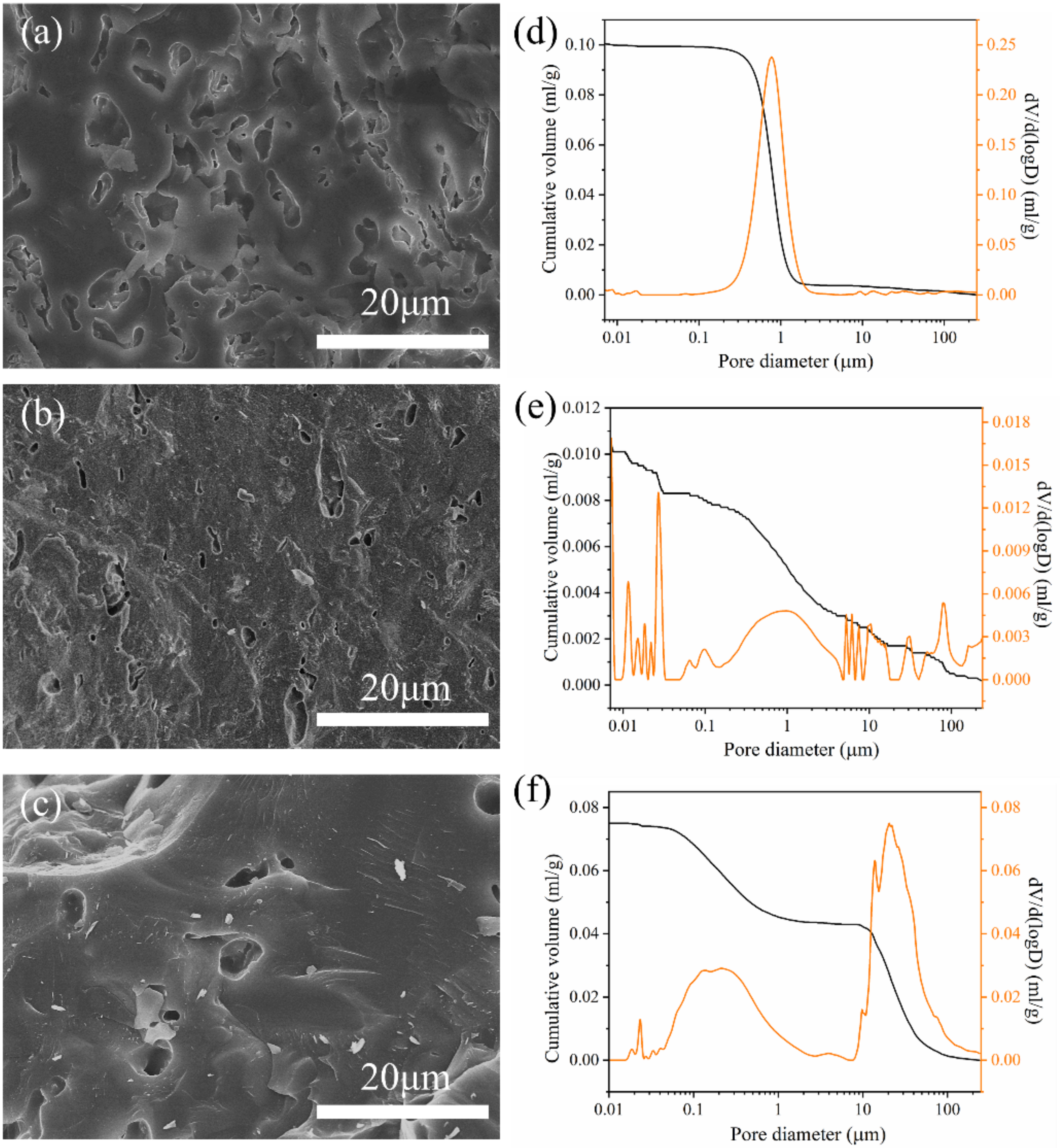

Figure 5

SEM images of (a) pottery, (b) Benshanzhu-Zisha, (c) porcelain; Pore size distributions determined by mercury porosimetry for (d) pottery, (e) Zisha, (f) porcelain.

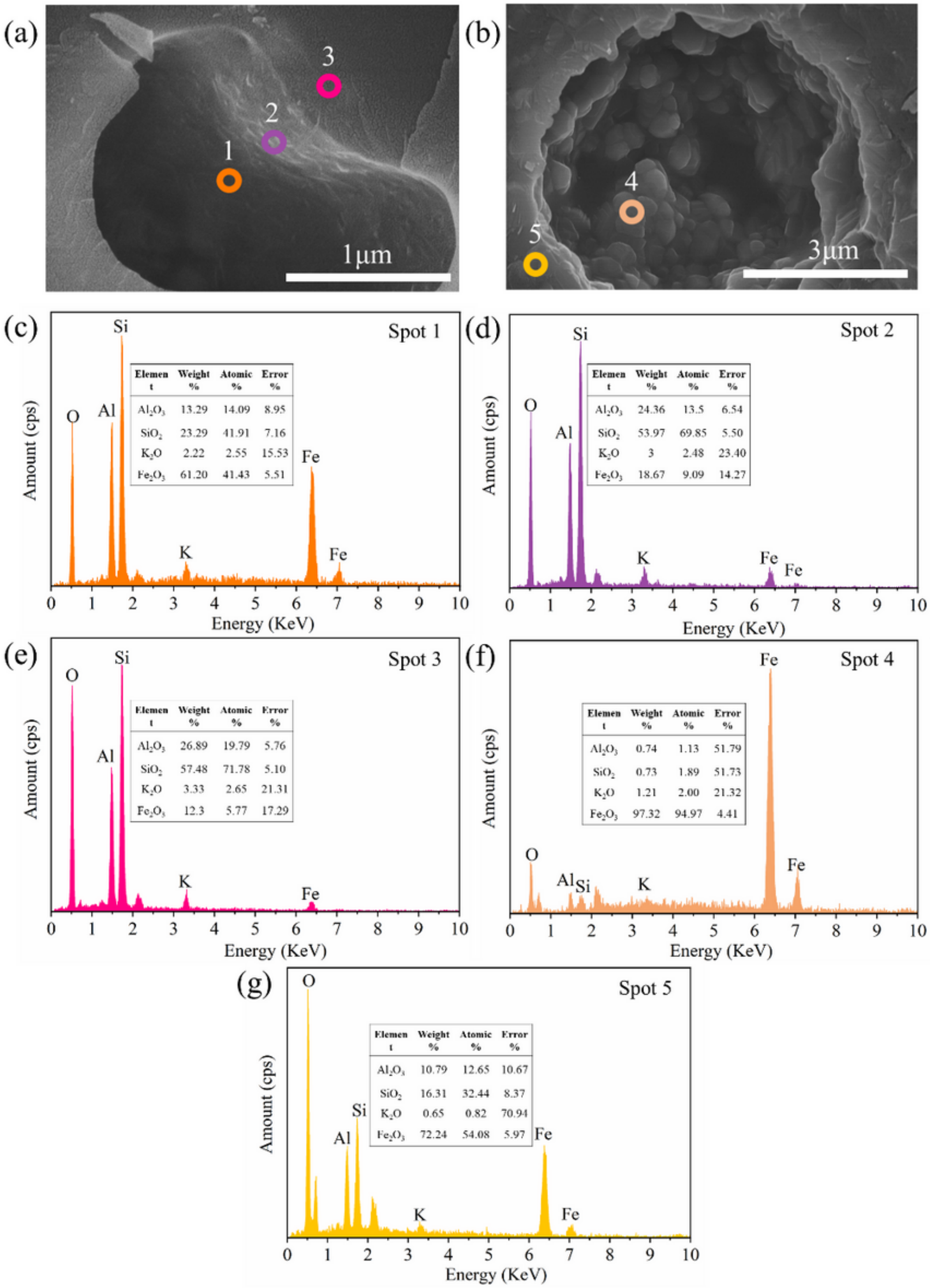

Figure 6

The EDS results of 5 spots in two typical pores for Benshanzhu-Zisha.