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The Compositions and Pore Structures of Benshanzhu Zisha Ceramics

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Abstract

Yixing Zisha ceramics are popular traditional tea-sets with a long history in China but there have seldom been studies exploring their compositions and microstructures. In this work, Benshanzhu-Zisha, a typical representative of Zisha clay from the city of Yixing in China, is investigated. The XRD results demonstrate that the Benshan Zhu clay is a natural mineral compound with a high content of hematite. 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 phase (10.7 wt%). Moreover, there are many dispersed and thin pores contained in the Benshanzhu-Zisha, ranging from nanometers to microns in size, and there are large numbers of hematite particles in the pores. It is the unique pore structures that make Benshanzhu-Zisha the perfect vessel for brewing tea, impermeable to water but gas "breathable".

Keywords: Zisha, traditional ceramics, Yixing, pore structures

I. Introduction

Yixing Zisha ceramics are regarded as the most representative and influential traditional tea-sets in ancient and contemporary China, especially for brewing tea [1]. Yixing Zisha ware has passed through a thousand years of history, and the technological process for making it has also been listed as one of the first national intangible cultural heritages of China. The unique charm of Zisha pottery has attracted the attention of scholars. Some have focussed on the artistry and cultural history of Zisha ware [2–4]. Several reports point out that its high porosity is the reason for its ability to perfectly brew tea [5,6]. Dicaoqing-Zisha pottery has recently been the subject of scientific research [7]. However, Zisha pottery is actually a very big family of ceramics with many members. Each member has its own particular features. It is worth exploring the compositions, microstructures and the relationship of each member of Zisha ceramics.

Yixing Zisha ceramics are made from different Zisha clays, the names of these clays being traditionally used to name the corresponding Zisha products. Different raw clays lead to wide 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 the Huanglong Mountain mining district, Yixing city, and Jiangsu Province, China, are collectively called "Benshan Clay". Zhu clay is a typical Red clay. Its ores are distributed between the red clay layer or shelf soil and tender clay ore layer, closer to the land surface. The thickness of the Zhu clay ore layer usually ranges from a few centimeters to several meters, because Zhu clay is weathered by the infiltration of surface rainwater into the tender clay to different degrees. The yield of Red clay is lower than that of Purple clay and Duan clay; furthermore, Zhu clay is a rare class of Red clay. Zhu clay from the Huanglong Mountain mine is 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 concerning the formation of the compositions and pore structures of Benshanzhu-Zisha are demonstrated with reference to the minerals contained in Benshanzhu clay. First, Benshanzhu clay is a natural mineral compound containing 24.1 wt% illite, 15.7 wt% kaolinite, 9.2 wt% montmorillonite, 9.3 wt% hematite and 10.1 wt% goethite. Second, compared with other porcelain and pottery clays, Benshanzhu-Zisha has the highest content of hematite (11.5 wt%) and amorphous phase (71.2 wt%) owing to the low content of Al_2O_3 but extremely high content of Fe_2O_3 in the clay. And the content of mullite in Benshanzhu-Zisha (10.7 wt%) is much lower than in other porcelain and pottery clays. Moreover, there are many dispersed and thin pores on the surface of Benshanzhu-Zisha, which have a wide pore size distribution ranging from micro- to nanoscale. In addition, there are large numbers of hematite particles in the pores. Benshanzhu-Zisha has unique pore structures that make the

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Zisha impermeable to water but "gas-breathable", i.e. the ideal vessel for brewing tea.

II. Materials and Methods

(1) Materials

Benshanzhu raw material was obtained from Dingshu town, Yixing city, Jiangsu province, China. The commercial-formula porcelain material in this work was purchased from Jingdezhen, China. The pottery consisted of an earthen pot purchased from a commodity market.

(2) Sample preparation

Before the Benshanzhu raw material was used to prepare a green body, it was selected, ground and sifted, before being aged by natural weathering for a few months. And then the aged material was processed by continuously pounding and crafting to form a green body. The sintering process for 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 at a rate of 3 K/min and held for 30 min, and then the temperature was raised from 300 °C to 700 °C at a rate of 7 K/min and held for 30 min. Finally, the samples were sintered from 700 °C to 1 180 °C at a rate of 5 K/min and held for 30 min.

The porcelain green body, cut from the commercial-formula porcelain material, was first fired from room temperature to 100 °C at a rate of 2 K/min and held for 30 min, then the temperature was increased to 200 °C at a rate of 2 K/min before being raised to 300 °C at a rate of 2 K/min, the two temperatures were each held for 30 min. After that, the temperature was raised from 300 °C to 600 °C at a rate of 8 K/min and then raised to 1 000 °C at the same rate; the two temperatures were held for 30 min. Finally, the porcelain sample was fired from 1 000 °C to 1 320 °C at a rate of 8 K/min and held for 30 min.

(3) Characterization

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

III. Results and Discussion

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

Fig. 3 shows the TG-DSC analysis of the 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

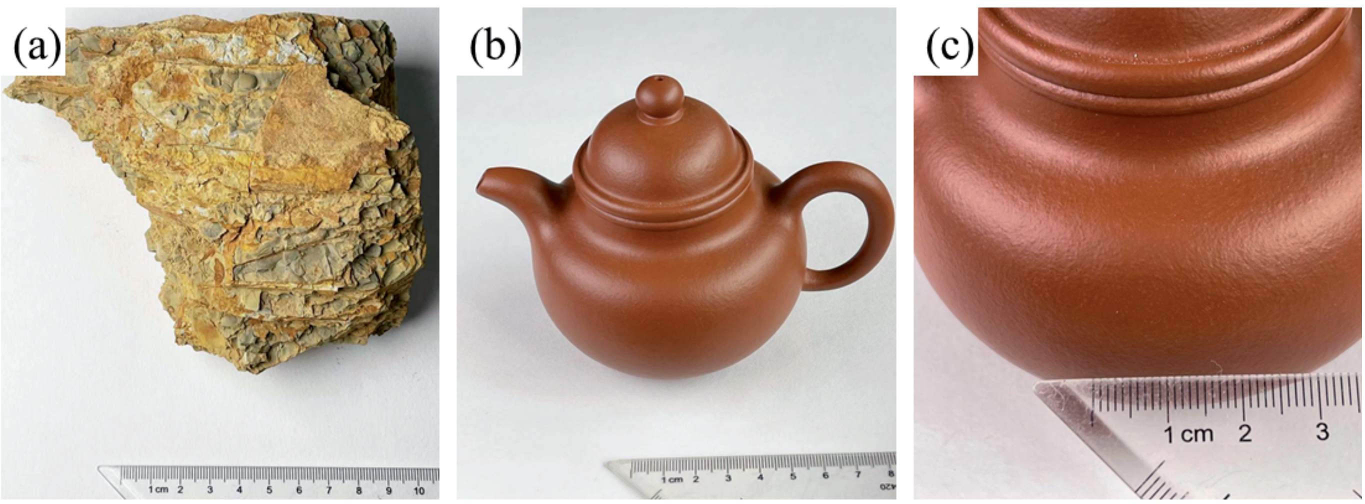

Fig. 1: Photograph of (a) Benshanzhu-Zisha raw material, (b) Benshanzhu-Zisha teapot and (c) close-up photograph of the surface.

Table 1: The mineral composition of the Benshanzhu-Zisha green body

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

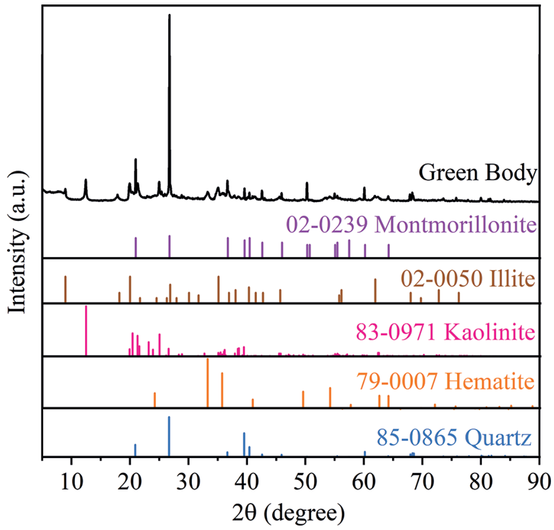

Fig. 2: XRD pattern of the Benshanzhu-Zisha green body.

loss of 9 %. Benshanzhu-Zisha green body has two clear endothermic valleys at about 245 °C and 450 °C, accompanied by a significant continuous mass loss, which results from the properties of the illite and montmorillonite [9] contained. 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 1 043 °C, which is ascribable to the new formation of crystalline phases during firing [13–15].

Table 2 shows the chemical compositions of the Benshanzhu-Zisha green body, porcelain and pottery. The mass percentage of Al_2O_3 in the Benshanzhu-Zisha green body, 19.53 wt%, is lower than that in the porcelain and pottery. This result should be ascribed to its low total mass percentage of clay minerals. The total content of alkali metal oxide and alkali earth metal oxides (K_2O + Na_2O + MgO + CaO) in the Benshanzhu-Zisha green body (3.35 wt%) is also lower than that in the porcelain (4.83 wt%) and pottery (7.35 wt%). But it is worth noting that Benshanzhu-Zisha green body has a much higher content of Fe_2O_3 than the other samples thanks to the rich hematite and goethite.

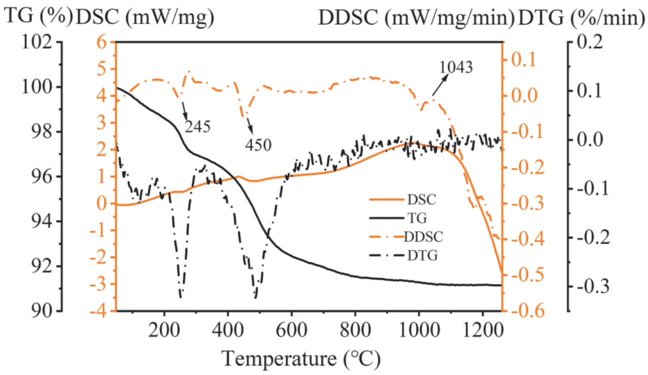

Fig. 3: TG-DSC analysis of the Benshanzhu-Zisha green body, the DTG and DDSC curves are the corresponding differential results.

The XRD patterns and quantitative analysis results of the Rietveld refinement for the fired porcelain, Benshangzhu-Zisha and pottery are also investigated (Table 3 and Fig. 4). The pottery consists of amorphous phase (52.9 wt%), mullite (22.0 wt%), quartz (16.6 wt%), anorthite (7.6 wt%) as well as cristobalite (0.5 wt%) and rutile (0.4 wt%). The pottery is usually fired at a low temperature (below 1 000 °C).

Table 2: Chemical composition of the 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

Table 3: The quantitative analysis results (wt%) of the Rietveld refinement for the 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

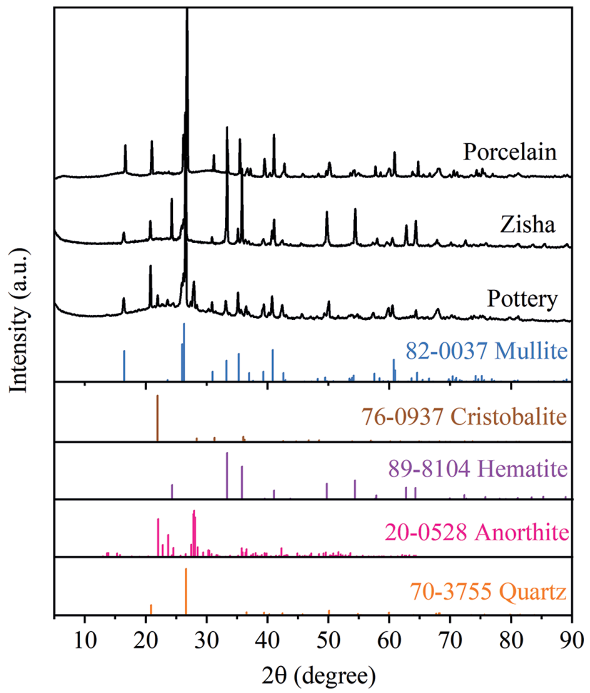

Fig. 4: XRD patterns of the porcelain, Benshangzhu-Zisha and pottery.

Therefore, its reactions during firing are not sufficient. Hence, we mainly compared the chemical composition and crystalline phases of the Benhsanzhu-Zisha with that of those of the porcelain. As shown in Table 3, the content of mullite in the Benshanzhu-Zisha (10.7 wt%) is much lower than in the porcelain (24.7 wt%) and pottery (22.0 wt%), but the Benshanzhu-Zisha has the highest content of hematite (11.5 wt%) and amorphous phase (71.2 wt%) of the three ceramics. The low content of mullite in the Benshanzhu-Zisha can be ascribed to the insufficient Al_2O_3. And the significantly high content of hematite and amorphous phase should be attributed to the very rich Fe_2O_3, which not only served as fluxing agent, but also plays an important role in the crystalline process. Although the total content of alkali metal oxide and alkali earth metal oxides in the Benshanzhu-Zisha is relatively low, it contains much higher Fe_2O_3 than in the porcelain and pottery, which contributes to the extensive melting of SiO_2 and Al_2O_3 and forming of large amounts of liquid phase. When firing ends, the formation of mullite only consumes a little SiO_2 owing to the limited content of Al_2O_3. Besides, the amount of quartz in the Benshanzhu-Zisha is also the lowest, 6.4 wt%. Finally, the residual liquid that contains very rich iron ions will be transformed to (1) the hematite and (2) the amorphous phase.

As shown in Fig. 5, the morphologies of the pottery, Benshanzhu-Zisha and porcelain presented significant differences. In Fig. 5a, the microstructure of the pottery contains lots of large and irregular pores with sharp corners, while in Fig. 5b, the Benshanzhu-Zisha is shown to contain many dispersed and thin pores. The pores in the porcelain shown in Fig. 5c are large and round in shape.

Furthermore, in order to explore the pore structure distributions in the pottery, Benshanzhu-Zisha and porcelain, we characterized their pore size distribution with mercury. The pore size distribution in the pottery, Benshanzhu-Zisha and porcelain is presented in Fig. 6. The pore size distribution of the pottery is mostly concentrated at 1 μm, whereas the Benshanzhu-Zisha shows a wide pore size distribution ranging from micro- to nanoscale. And the pores in the porcelain are mainly at around 0.2 μm and dozens of microns, with a relatively sparse distribution. The pore size distribution of the Benshanzhu-Zisha is more complicated than that in the pottery and porcelain. Hence, the Benshanzhu-Zisha has a unique and complicated microstructure.

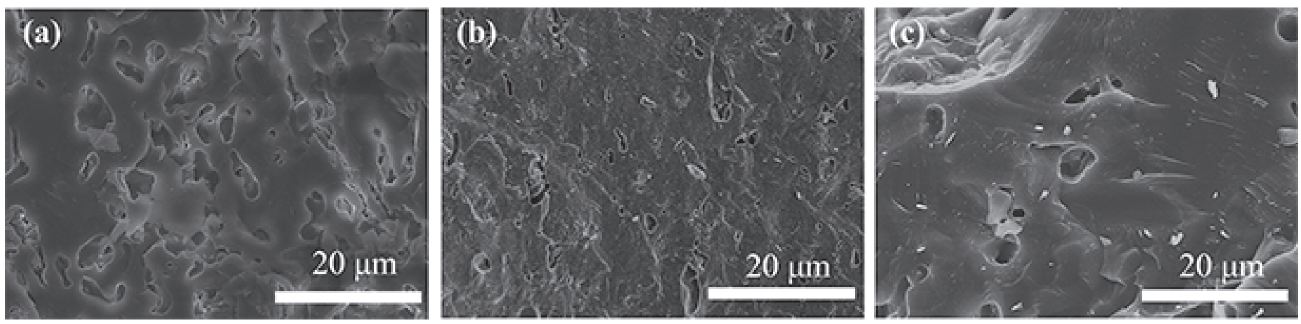

Fig. 5: SEM images of (a) pottery, (b) Benshanzhu-Zisha, (c) porcelain.

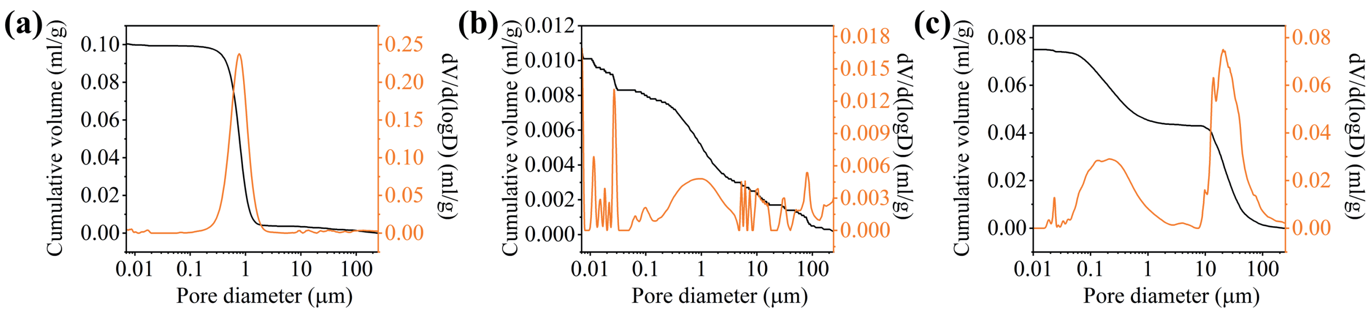

Fig. 6: Pore size distributions determined with mercury porosimetry for (a) pottery, (b) Zisha, (c) porcelain.

Table 4 shows the porosity characterizations of the porcelain, Benshanzhu-Zisha, and pottery. The porosity characterizations are tested by means of mercury porosimetry and BET measurement. When measured with mercury porosimetry, the Benshanzhu-Zisha exhibits the lowest porosity, pore volume and specific surface area compared with the porcelain and pottery, however, there is a large improvement in the data when the porosity is measured with BET. The pore volume and specific surface area of Benshanzhu-Zisha are still lower than those of the pottery, but higher than those of the porcelain. It is known that BET measurement depends on nitrogen absorption and desorption in the pores while mercury porosimetry depends on the filling of mercury into the pores. The liquid mercury can readily fill into large pores on micron level, but it is more difficult for the mercury to get into the tiny pores smaller than several nanometers. In contrast, the BET method based on the adsorption-desorption of gas is more accurate for the measurement of mesoporous to micropores, which usually measure less than 100 nm in diameter. It is almost incapable of recognizing larger pores measuring several microns. Compared with the porcelain, it is difficult for mercury to fill into the thin pores of the Benshanzhu-Zisha, while the filling of gas is not affected. No matter which method is chosen, the pottery shows higher pore volume and specific surface area than the porcelain and Benshanzhu-Zisha, which could be attributed to its many large pores.

Moreover, more specific microstructures of Benshanzhu-Zisha were investigated. The morphologies of two typical pores can be seen in Fig. 7(a) and 7(b). We analyzed the EDS results of five spots of the two typical pores to further determine their characteristics, Spots 1 – 3 for Pore 1 in Fig. 7(a) and Spots 4 and 5 for Pore 2 in Fig. 7(b). The inner wall of Pore 1 is smooth without obvious particulate matter. According to the EDS results for Spots 1 – 3, the contents of SiO_2 and Al_2O_3 are increased gradually from Spot 1 to Spot 3, while the content of Fe_2O_3 is dramatically decreased. The iron ions are mainly concentrated in the pores. Compared with Pore 1, there is lots of particulate matter in Pore 2. The EDS result for Spot 4 clearly shows the composition of the particulate matter, it is Fe_2O_3. Therefore, this particulate matter consists of hematite crystals. Spot 5 outside 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, the 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 tend to flow to the nearby liquid spots. At the same time, the pottery possesses good contents of alkali metal oxide and alkali earth metal oxides, which facilitate the formation of liquids. But the firing was ended early owing to the low firing temperature, and all reactions were ended abruptly. After crystallization and amorphization, plenty of large pores are formed at the sites of early liquid and maintain the shapes of the early liquids. As for the porcelain, it was fired at 1 300 °C, and has sufficient K_2O + Na_2O + MgO + CaO, the liquids would flow throughout the body [16]. After complete crystallization, the residual liquid with low viscosity filled the pores and formed the amorphous phase. A few large pores may be bubbles that remained in the liquid. Thereby, the porcelain is dense and the pores in the porcelain are round, and present in a much lower quantity than in the pottery and Zisha. Benshanzhu-Zisha was fired at a medium temperature (1 180 °C) compared with the pottery and porcelain. At the same time, it contains considerable liquid during firing owing to the very rich Fe_2O_3. The EDS results support our speculation that Fe_2O_3 plays an important role in the 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, liquid with so 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 for their capability for fluxing and reducing viscosity [17]. After firing, the pores from ignition loss will be partly filled by crystalline and amorphous phase generated from liquids, but the pores cannot be completely filled because the liquids are unable to flow to all pores on account of their high viscosity. Hence, many thin pores survive. In addition, the EDS analysis reveals that iron ions have two places to go: one is to form hematite and the other is to remain in the amorphous phase. Accordingly, the pores of the Benshanzhu-Zisha exhibit two typical morphologies: one shows a smooth inner wall, the other contains many hematite particles. It is obvious that the hematite crystals can narrow the pores and form an uneven inner wall, which makes it difficult for the mercury to fill the pores but permits the gas to pass through. This result is in accordance with the porosity of the Benshanzhu-Zisha shown in Table 4, which also accounts for the good gas breathability, but no water seepage of Zisha ceramics.

Table 4: Characterization of the porosity of the porcelain, Benshanzhu-Zisha, and pottery.

	Porosity (vol%) by mercury porosimetry	Pore volume (ml/g) by mercury 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

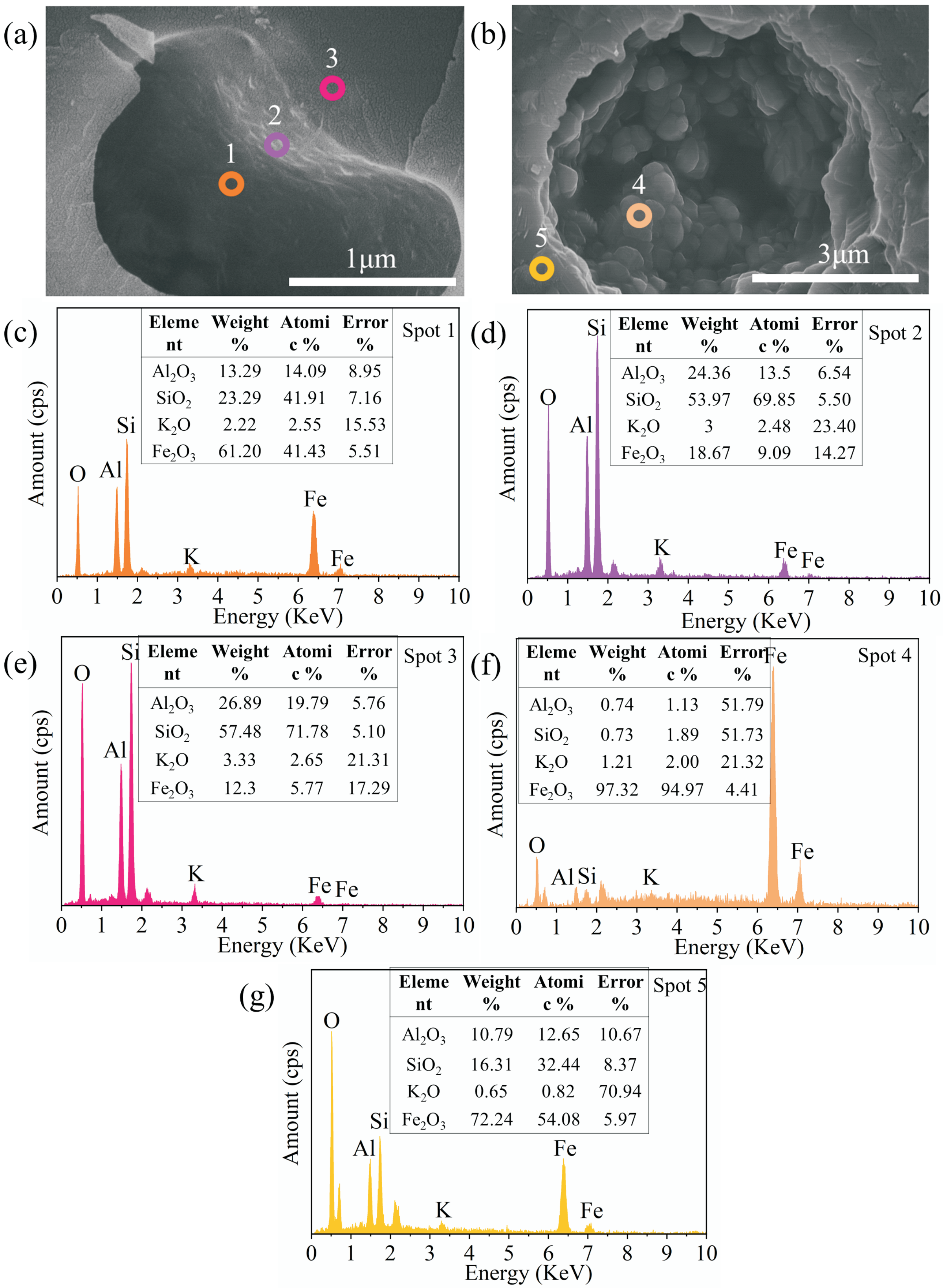

Fig. 7: The EDS results for five spots in two typical pores for Benshanzhu-Zisha.

IV. Conclusions

Benshanzhu-Zisha ceramic has been investigated, with analysis of the mineral compositions of its raw materials, crystalline compositions and pore structures. Benshanzhu-Zisha clay is a natural mineral compound, which consists of 24.1 wt% illite, 15.7 wt% kaolinite, 9.2 wt% montmorillonite, 9.3 wt% hematite and 10.1 wt% goethite. The content of mullite in the Benshanzhu-Zisha (10.7 wt%) is much lower than that in the porcelain (24.7 wt%) and pottery (22.0 wt%) tested, but the Benshanzhu-Zisha has the highest content of hematite (11.5 wt%) and amorphous phase (71.2 wt%) of the three ceramics owing to its low content of Al_2O_3 but extremely high content of Fe_2O_3 in 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- to nanoscale. Moreover, there are large numbers of hematite particles in the pores. The unique pore structures endow it with good gas "breathability" but no water seepage, which accounts for its reputation for perfect tea-sets.

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References

1 Fang, J.J., Fei, Y.Y.: A brief introduction to the aesthetic features of zisha pottery, *Jiangsu Ceramics*, **12**, 39 – 41, (2006).

2 Lee, V., Attinger, D.: Thermodynamics and historical relevance of a jetting thermometer made of chinese zisha ceramic, *Sci. Rep.*, **6**, 28609 (2016).

3 Zhu, J., MacDonald, B.L., Hang, T., Zhu, Z.W.: Glascock MD. compositional characterization of zisha clay from the yixing area (Jiangsu, China) by neutron activation analysis, *Microchem. J.*, **147**, 1117 – 1122 (2019).

4 Wu, J., Hou, T., Zhang, M.L., Li, Q.J., Wu, J.M., Li, J.Z., Deng, Z.Q.: An analysis of the chemical composition, performance and structure of china yixing zisha pottery from 1573 A.D. to 1911 A.D., *Ceram. Int.*, **39**, 2589 – 2595, (2013).

5 Chung, T.Y., Kuo, P.C., Liao, Z.H., Shih. Y.E., Yang, M,L,, Cheng, M.L., Wu, C.C., Tzen, J.T.C.: Analysis of lipophilic compounds of tea coated on the surface of clay teapots, *J. Food Drug Anal.*, **23**, 71 – 81, (2015).

6 Liao, Z.H., Chen, Y.J., Tzen, J.T., Kuo, P.C., Lee, M.R., Mai, F.D., Rairate, T., Chou, C.C.: Effect of teapot materials on the chemical compositions of oolong tea infusion, *J. Sci. Food Agric.*, **98**, 751 – 757, (2018).

7 Yang, C.R., Kong, J.Y., Yang, J.J., Chu, C.L., Wang, X.D., Li, Y.B.: The study of crystal-phase composition and pore structure for dicaoqing-zisha compared with porcelain and pottery, *Ceram. Int.*, (2020).

8 Zhu, Z.W., Shen, Y.Q.: Yixing Zisha mineral. Geological Publishing House; Beijing, 2009, in Chinese.

9 Mcconville, C.J., Lee, W.E.: Microstructural development on firing Illite and Smectite clays compared with that in Kaolinite. *J. Am. Ceram. Soc.*, **8**, 2267 – 2276, (2010).

10 Lee, W.E., Souza, G.P., Mcconville, C.J.: Taevornpanich T, Iqabal Y. Mullite formation in clays and clay-derived vitreous ceramics. *J. Eur. Ceram. Soc.*, **28**, 465 – 471, (2008).

11 Lao, X.B., Xu, X.Y., Jiang, W.H., Liang, J., Miao, L.F., Wu, Q.: Influences of impurities and mineralogical structure of different kaolin minerals on thermal properties of cordierite ceramics for high-temperature thermal storage. *Appl. Clay Sci.*, **187**, 105485, (2020).

12 Abd Aziz, M.H., Othman, M.H.D., Hashim, N.A., Adam, M.R., Mustafa, A.: Fabrication and characterization of mullite ceramic hollow fiber membrane from natural occurring ball clay, *Appl. Clay Sci.*, **177**, 51 – 62, (2019).

13 Chin, C.L., Ahmad, Z.A., Sow, S.S.: Relationship between the thermal behaviour of the clays and their mineralogical and chemical composition: Example of Ipoh, Kuala Rompin and Mersing (Malaysia). *Appl. Clay Sci.*, **143**, 327 – 335, (2017).

14 Kamseu, E., Leonelli, C., Boccaccini, D.N., Veronesi, P., Miselli, P., Pellacani, G., Melo, U.C.: Characterisation of porcelain compositions using two china clays from Cameroon. *Ceram. Int.*, **33**, 851 – 857, (2007).

15 Gualtieri, A.F.: Thermal behavior of the raw materials forming porcelain stoneware mixtures by combined optical and in situ X-Ray dilatometry. *J. Am. Ceram. Soc.*, **90**, 1222 – 1231, (2007).

16 Dong, W.X., Bao, Q.F., Zhou, J.E., Zhao, T.G., Liu, K., Li, S.Z., Liu, S.Y., Ma, K.X.: Comparison and low-temperature sintering mechanism of "K_2O-Na_2O" and "Li_2O-K_2O-Na_2O" fluxes, *J. Ceram. Soc. Jpn.*, **128**, 821 – 831, (2020).

17 Bahgat, M., Abdel Halim, K.S., El-Kelesh, H.A., Nasr, M.I.: Metallic iron whisker formation and growth during iron oxide reduction: K_2O effect, *Ironmak. Steelmak.*, **36**, 379, (2009).