

Comparison of the Composition and Pore Structure of Four Common Zisha from Yixing City after Firing

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Abstract

Zisha teapots are the most famous among the multitude of types of pottery made in China. The high porosity of Zisha teapots may be the reason for their perfect effect in tea brewing. However, there are many types of Zisha (including purple clay, red clay, and Duan clay), and their chemical composition, phase composition and pore structure may also vary. Here, we investigated the relationship between the composition and pore structure of four types of Zisha. The pore distribution of Qingshuini Zisha (QSN-ZS) and Qinghui-Duan Zisha (QHD-ZS) in the range of 0.02–3 μm far exceeds that of the other two Zisha. Meanwhile, QSN-ZS and QHD-ZS also have higher porosity. The porosity is related to the content of Fe_2O_3 , and a medium content (2.5 wt%–5 wt%) of Fe_2O_3 is beneficial for high porosity.

Keywords: Zisha, composition, pore structure, hematite.

I. Introduction

China has a long history of pottery, dating back to at least ~20 000 years ago¹. As a special type of pottery, Zisha (purple sand) pottery has been produced in China since the Song dynasty (960 AD to 1279 AD) and is abundant in Yixing City, China^{2–5}. In addition to Zisha, Yixing is also rich in tea. The development of the tea-drinking culture provided a foundation for the emergence and development of tea sets in Yixing. As a representative of Yixing tea sets, the Zisha teapot can be dated back to Zhengde period (1506 AD to 1521 AD) of the Ming Dynasty⁶. It is recognized as one of the best tea sets for its characteristic of preventing tea from discoloration and spoilage⁷. The physical and cultural characteristics of the Zisha teapots perfectly match with Chinese tea culture, leading to its continuous innovation and development.

Some efforts have been made to reveal the reasons for the excellent performance of Zisha teapots in brewing tea. Liao *et al.* investigated the effect of Zisha teapots on the chemical composition of tea^{7, 8}. By comparing the chemical composition of oolong tea brewed in teapots made of different materials including Zisha, stainless steel, ceramics, glass and plastic, they found that the content of the beneficial substances was higher in the tea brewed in the Zisha teapots. This is of great health significance for long-term tea drinkers. They observed the surface of the teapots by means of scanning electron microscopy and found that, unlike glass and porcelain teapots, the surface of the Zisha teapot contained 0.01- to 0.02-mm cavities. Thus, they attributed the good performance of Zisha in tea brewing to its porosity. Wu *et al.* analyzed the fragments of Zisha pro-

duced from 1573 AD to 1911 AD and also pointed out that the high porosity of Zisha may be the reason for its perfect effect in tea brewing⁹.

There are many varieties of Zisha clays, commonly including purple clay, red clay, and Duan clay, among which the yield of red clay is lower by comparison¹⁰. Yang *et al.* investigated the correlation between the composition and pore structures of Dicaoqing Zisha (a class of purple clay) and Benshanzhu Zisha (a class of red clay)^{10, 11}. The main crystal components of Benshanzhu Zisha were hematite, quartz, and mullite, while the content of hematite in Dicaoqing Zisha is lower. The porosity of Dicaoqing Zisha and Benshanzhu Zisha they measured were 14.53 and 2.85 vol%, respectively. It can be seen that there are significant differences in the chemical composition of different varieties of Zisha, which can also affect their pore structures and porosities.

However, research on composition and pore structure of different varieties of Zisha is still relatively limited. Here, we investigated four common Zisha clays from Yixing City, including two purple clays (Qingshuini clay and Zini clay) and two Duan clays (Huang-Duan clay and Qinghui-Duan clay). The correlation between composition and pore structure will be revealed based on comparison of the different Zisha samples.

II. Experimental

Materials: The raw materials of Qingshuini clay, Zini clay, Huang-Duan clay, Qinghui-Duan clay were obtained from Dingshu Town, Yixing City, Jiangsu Province, China.

Sample preparation: Each raw material was first selected and crushed, and then aged by means of natural weath-

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ering for several months. The aged material was screened, ground and mixed with water. And the mud was made into the green body by continuously beating and kneading. The green body was cut into approximately 2 cm × 2 cm pieces. The four green bodies were named as Qingshui-ni clay (QSN), Zini clay (ZN), Huang-Duan clay (HD), Qinghui-Duan clay (QHD). They were dried in an oven at 80 °C for 24 hours, and then fired in an electric kiln. The four samples were fired simultaneously, and the steps were as follows: The samples were heated from room temperature to 100 °C in 30 minutes, and then the temperature was raised to 300 °C in 90 minutes. The temperature was increased from 300 °C to 500 °C in 60 minutes, and then further to 900 °C in 150 minutes. Finally, it took 80 minutes to increase the temperature to 1 160 °C. The samples were kept at 1 160 °C for 40 minutes and then cooled naturally. After firing, the four Zisha samples were named as QSN-ZS, ZN-ZS, HD-ZS, QHD-ZS.

Characterization: The morphology and chemical analysis was performed using a Hitachi SU1510 scanning electron microscope (SEM) equipped with Oxford energy dispersive X-ray apparatus (EDX). Powder X-ray diffraction (XRD) patterns were analyzed with a Rigaku Ultima IV X-ray diffractometer using CuK α radiation as the X-ray beam source. Porosity was determined with the mercury intrusion method by using the Micromeritics AutoPore V 9620 equipment. The bulk density (ρ_{bulk}) and apparent density (ρ_{apparent}) were calculated according to:

$$\rho_{\text{bulk}} = \frac{m}{V_{\text{total}}} \quad (1)$$

$$\rho_{\text{apparent}} = \frac{m}{V_{\text{total}} - V_{\text{open}}} \quad (2)$$

where m is the mass of the sample, V_{total} is the total volume of the sample (including all pores), V_{open} is open pore volume measured with the mercury intrusion porosimeter.

III. Results and Discussion

Photographs of the four Zisha green body samples before and after drying at 80 °C for 24 hours are shown in Fig. 1. The color of the green body samples before drying is relatively bright, while the color becomes darker after drying. At the same time, it can be seen that there are significant differences in the color of different Zisha green body samples, indicating that their composition is different. This has also been verified by means of XRD, as shown in Fig. 2. The crystalline peaks in the spectra can be referred to quartz, kaolinite, hematite, illite, anatase and rutile^{10–15}. The peak intensity of quartz in each spectrum is the strongest.

The mineral weight percentages of the four Zisha green body samples were obtained with the Rietveld method using GSAS-II software, and the Rietveld refinement results are shown in Table 1^{16,17}. The weight percentage of quartz (JCPDS 70–2517)¹¹ in each sample is the highest, exceeding 50 wt%. Next are illite (JCPDS 70–3754)¹² and kaolinite (JCPDS 83–0971)¹⁰, with a combined weight percentage of 28 to 38 wt%. A small amount of anatase (JCPDS 71–1166)¹³ is also found in each Zisha green body sample, while rutile (JCPDS 83–2242)¹⁴ only appears in the Huang-Duan clay. Hematite (JCPDS 89–8104)¹⁵ is an important component of Zisha, with high content in both Benshanzhu and Dicaqing Zisha green bodies^{10,11}. Among the four Zisha green body samples we selected, the weight percentage of hematite in ZN is the highest, with a value of 7.9 wt%. It is worth noting that according to the XRD refinement results, there is no hematite in HD. To avoid miscalculation of the GSAS-II software, we zoomed in the XRD patterns (Fig. 3). It can be observed that there is no obvious peak in the XRD spectrum of the Huang-Duan clay near 33.2 degree where the main peak of hematite is located¹⁵. This validates the results of the XRD refinement. The elemental analysis results of the four Zisha green body samples are shown in Table 2. Among the four samples, the iron content of HD is the lowest and the titanium content is the highest, which is consistent with the content of hematite and crystalline TiO₂ in XRD.

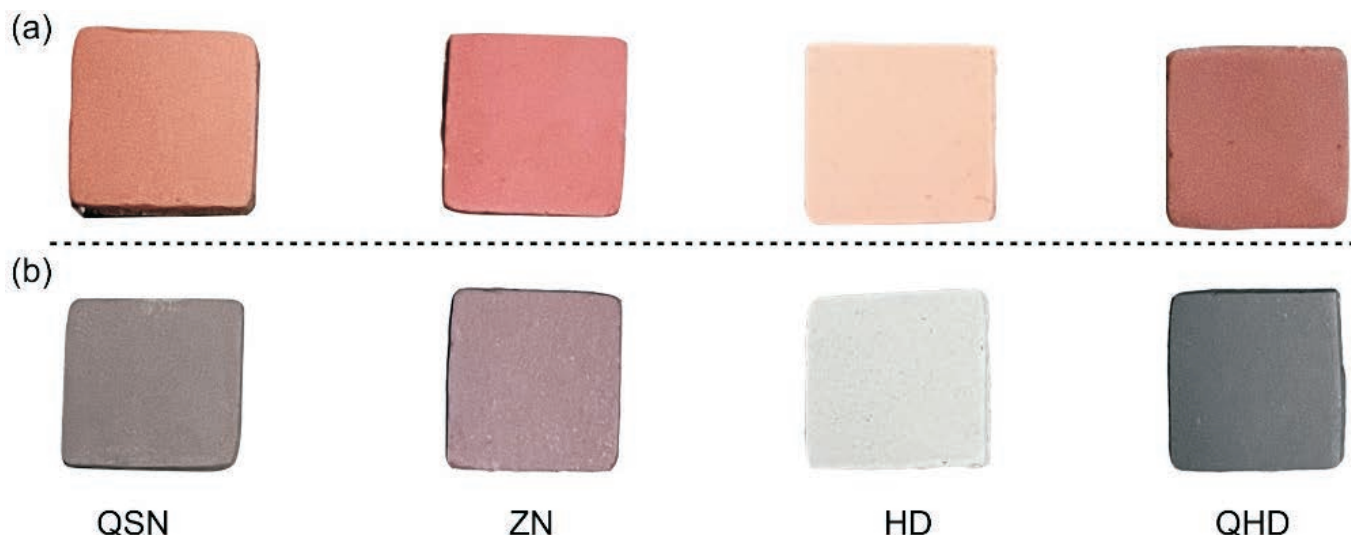


Fig. 1: Photographs of the four Zisha green body samples (a) before and (b) after drying at 80 °C for 24 hours.

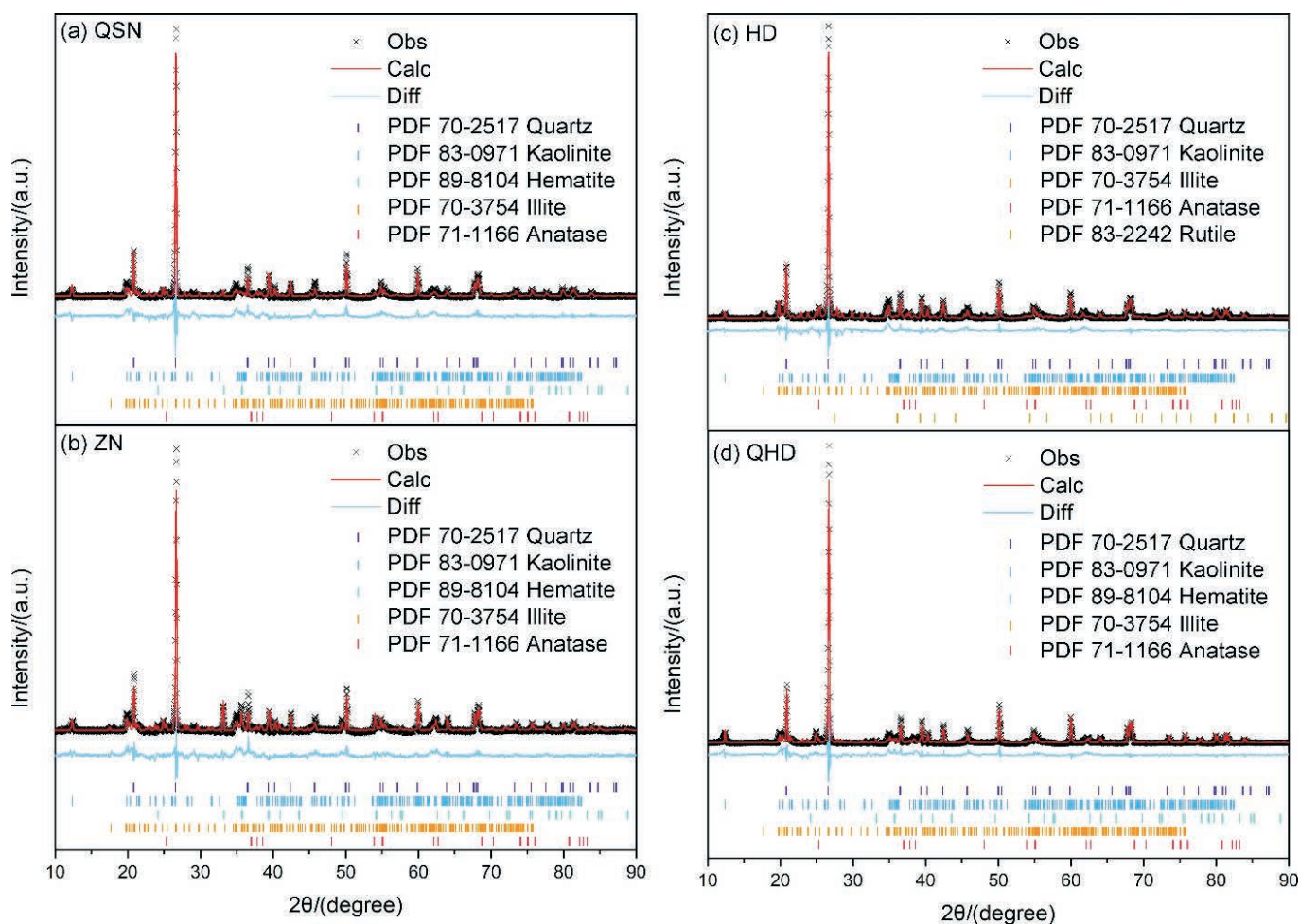


Fig. 2: XRD patterns of the four Zisha green body samples.

Table 1: The quantitative analysis results (wt%) of the Rietveld refinement for the four Zisha green body samples.

	QSN	ZN	HD	QHD
Quartz	63.6	53.8	59.9	69.1
Kaolinite	16.4	15.0	6.4	15.0
Illite	17.0	21.2	31.2	13.4
Hematite	1.9	7.9	-	1.3
Anatase	1.1	0.5	1.9	1.2
Rutile	-	-	0.6	-

Table 2: Elemental analysis results (wt%) of the four Zisha green body samples.

	QSN	ZN	HD	QHD
Si	17.12	20.4	30.76	32.69
O	67.03	62.37	60.88	60.18
Al	14.45	11.98	3.54	6.12
Fe	0.59	3.52	0.28	0.62
Ti	0.12	0.13	3.67	0.11
K	0.57	1.13	0.87	0.17
Ca	0.12	0.47	-	0.1

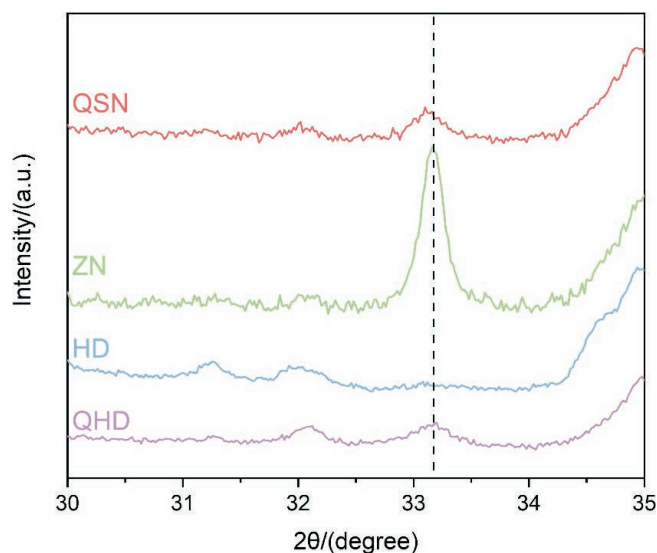


Fig. 3: Partially magnified XRD patterns of the four Zisha green body samples.

An important factor for the formation of Zisha products is the firing temperature, usually ranging from 1050 to 1200 °C^{5,9-11}. We used 1160 °C as the firing temperature. To avoid any impact of the firing process, all Zisha pieces were fired together in the electric kiln. After firing, the four Zisha pieces become bright again (Fig. 4). The colors of the fired QSN-ZS, ZN-ZS, HD-ZS, QHD-ZS are dark red, dark purplish red, yellow, and coffee

respectively. At the same time, it can be observed that there are small dots of different colors distributed on each piece, indicating that the composition of the fired Zisha is not uniformly distributed. Therefore, before performing XRD testing, we crushed and ground the Zisha pieces to reduce errors caused by uneven distribution of the phase composition.

The XRD patterns and the quantitative analysis results of the Rietveld refinement for the four Zisha samples after firing are shown in Fig. 5 and Table 3. The main mineral phases of the four fired Zisha samples are quartz and mullite (JCPDS 82–0037)¹⁰. The content of quartz and mullite in the products obtained from the QSN-ZS and ZN-ZS is similar, while the content of quartz in the products obtained from the HD-ZS and QHD-ZS is higher than that of mullite. ZN-ZS has the highest content of hematite (14.8 wt%), followed by the QSN-ZS (4.6 wt%) and QHD-ZS (2.9 wt%), and no hematite is detected in the HD-ZS. This is consistent with the XRD results before firing. Cristobalite (JCPDS 82–0512)¹¹ is also detected in QSN-ZS (5.0 wt%), ZN-ZS (0.8 wt%) and QHD-ZS (5.9 wt%), but not in the HD-ZS. Another noteworthy thing is that although crystalline TiO_2 (mainly anatase or rutile) is present in all four green bodies, crystalline TiO_2 (rutile, 1.2 wt%) was only found in the HD-ZS after firing.

Table 3: The quantitative analysis results (wt%) of the Rietveld refinement for the four Zisha samples after firing.

	QSN-ZS	ZN-ZS	HD-ZS	QHD-ZS
Quartz	46.4	40.2	70.6	52.0
Mullite	44.0	44.2	28.2	39.1
Hematite	4.6	14.8	-	2.9
Cristobalite	5.0	0.8	-	5.9
Rutile	-	-	1.2	-

Figs. 6 (a)–(d) presents the SEM images of top surfaces of the four fired Zisha pieces. It can be seen that the surfaces of QSN-ZS and HD-ZS have significant undulations, while the surfaces of ZN-ZS and QHD-ZS are relatively flat. Meanwhile, all the four fired Zisha pieces have many

pores on their surfaces. In order to see the microstructure of the pores more clearly, the pore structure was observed at high magnification, as shown in Figs. 6 (e) – (h). The pore size ranges from 0.4 to 20 μm in the SEM images. At the same time, it can be seen that the surface of the pores is not smooth, which leads to a larger specific surface area. This will be beneficial for the effect of Zisha tea sets on the tea infusion.

In order to obtain the detailed distribution of pore size, mercury intrusion porosimetry (MIP) was carried out, as shown in Fig. 7. It can be seen that the pore sizes of all the four Zisha samples have two distribution ranges, namely 0.02–3 μm and > 40 μm . The pore distribution differences of the four Zisha in the range > 40 μm are relatively small, and the main peak in this range appears between 200 and 260 μm . The QSN-ZS and QHD-ZS exhibit a monomodal pore size distribution in the range of 0.02–3 μm , with a peak position of approximately 0.83 μm . ZN-ZS has a main peak at 0.15 μm and a shoulder peak at approximately 0.43 μm in this range. HD-ZS shows a bimodal distribution in the range of 0.02–3 μm with peaks at about 0.18 μm and 1.05 μm . In addition to the pore size peaks mentioned above, there are also some other secondary peaks, among which the most obvious one is the peak at 10 μm in ZN-ZS. From the distribution of pore size peaks, it can be seen that the proportion of pores in the range of 0.02–3 μm for QSN-ZS and QHD-ZS far exceeds that of ZN-ZS and HD-ZS. Meanwhile, the porosity and pore volume of QSN-ZS and QHD-ZS are higher (Table 4). Yang *et al.* pointed out that the porosity is related to the content of Fe_2O_3 ^{10,11}. The content of Fe_2O_3 in the porcelain, pottery, Dicaoqing Zisha and Benshanzhu Zisha they tested increased gradually, while the pottery and Dicaoqing Zisha have higher porosity. It can be seen that a medium content of iron oxide is beneficial for high porosity. The Fe_2O_3 content in the Zisha we selected is in the following order: HD-ZS < QSN-ZS, QHD-ZS < ZN-ZS. And the porosity of QSN-ZS and QHD-ZS is higher among the four samples. Therefore, our experimental results indicate that a medium content (2.5 wt%–5 wt%) of Fe_2O_3 helps to improve the porosity of Zisha. The apparent (skeletal) densities of the four fired Zisha samples are almost the same, about 2.5 g/mL. And the bulk densities of QSN-ZS and QHD-ZS are smaller because of their high porosity.

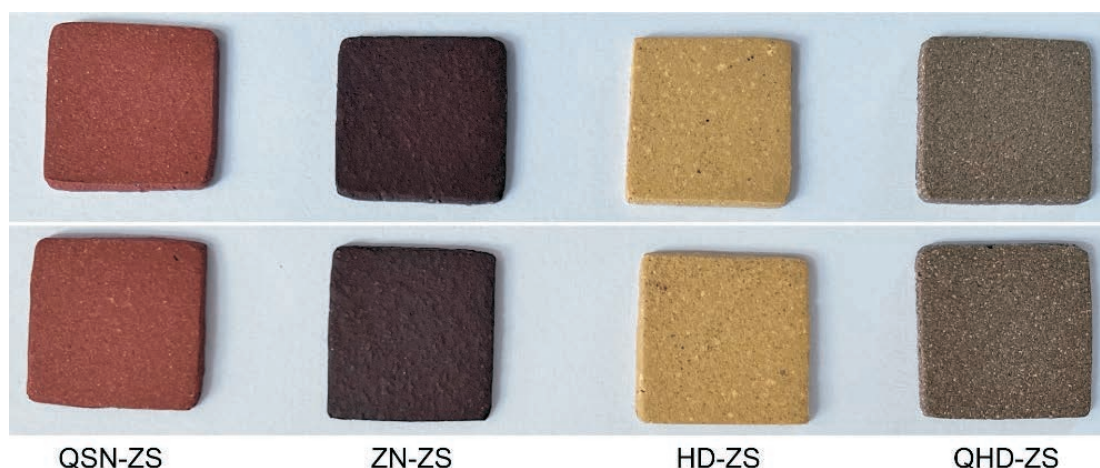


Fig. 4: Photographs of the four Zisha samples after firing. Two different pieces were selected for each kind of Zisha.

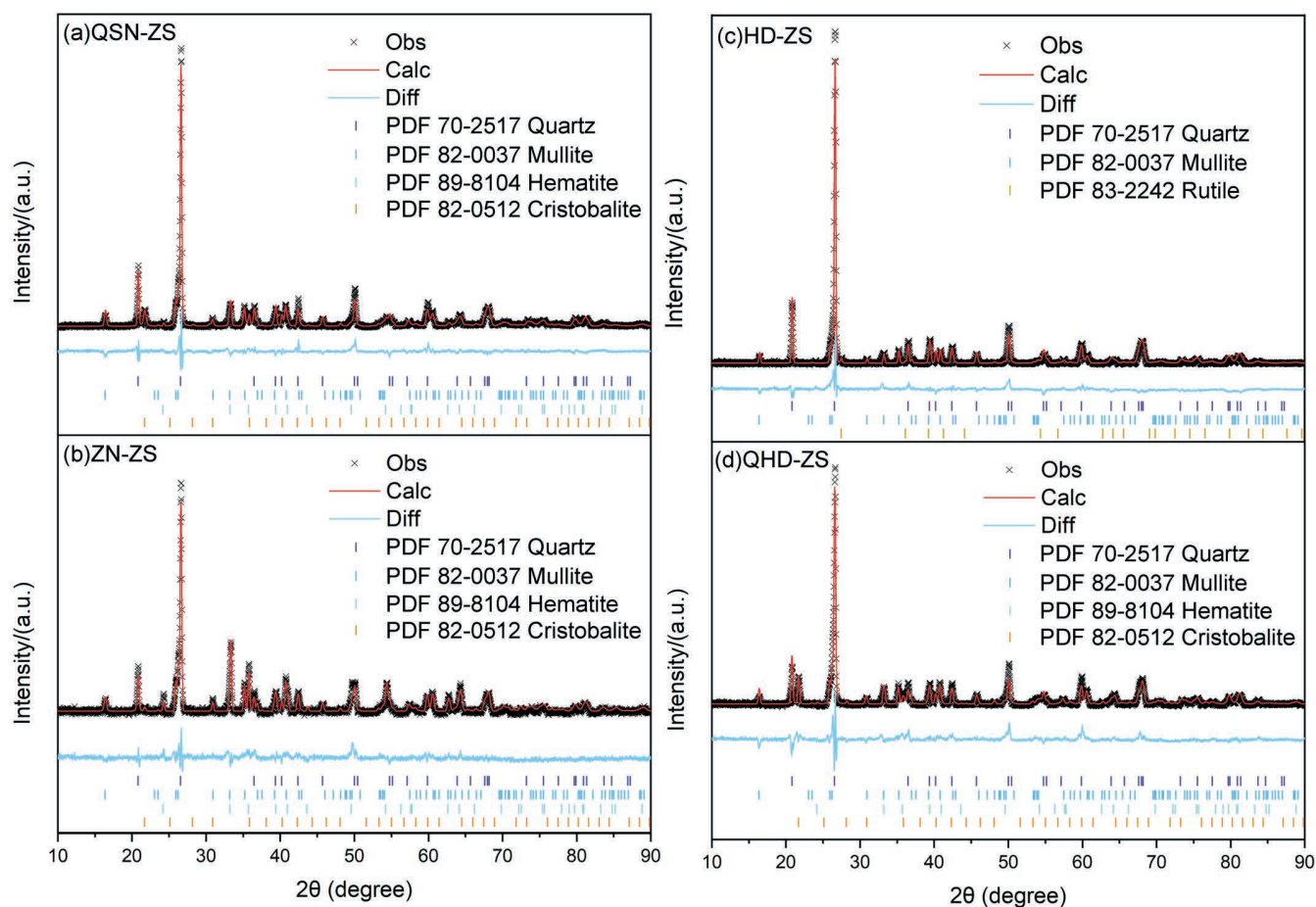


Fig. 5: XRD patterns of the four Zisha samples after sintering.

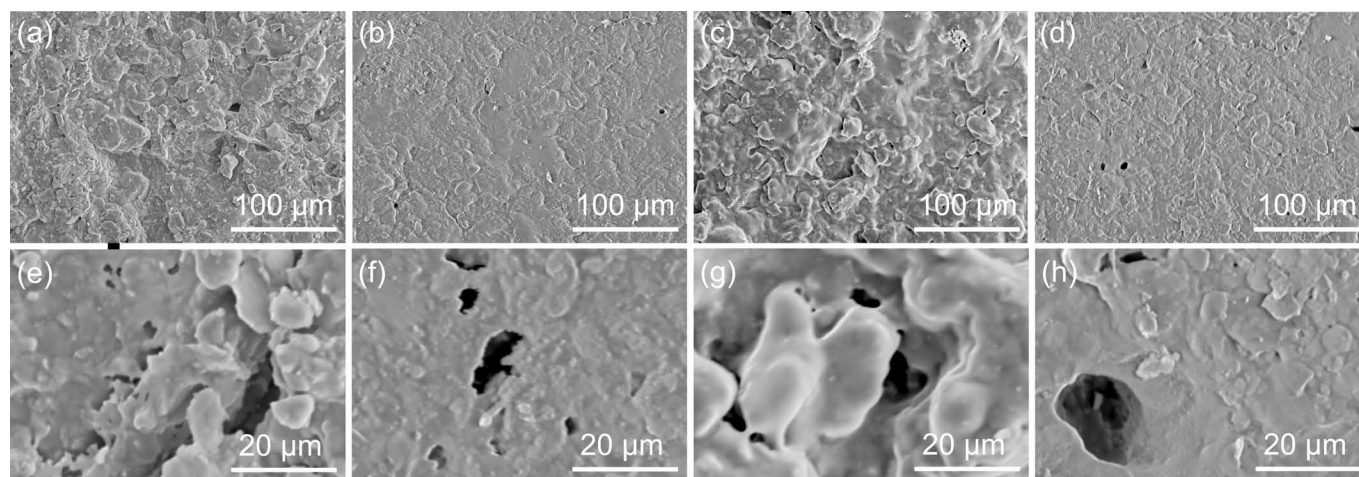


Fig. 6: SEM images of (a, e) QSN-ZS, (b, f) ZN-ZS, (c, g) HD-ZS, (d, h) QHD-ZS samples after firing at different magnifications.

Table 4: Porosity characterizations of the four Zisha samples after firing.

	QSN-ZS	ZN-ZS	HD-ZS	QHD-ZS
Porosity (vol%)	13.58	7.21	7.18	14.94
Pore volume (ml/g)	0.0628	0.0302	0.0316	0.0685
Pore area (m ² /g)	0.492	0.453	0.484	0.573
Bulk density (g/mL)	2.16	2.38	2.27	2.18
Apparent density (g/mL)	2.50	2.57	2.45	2.57

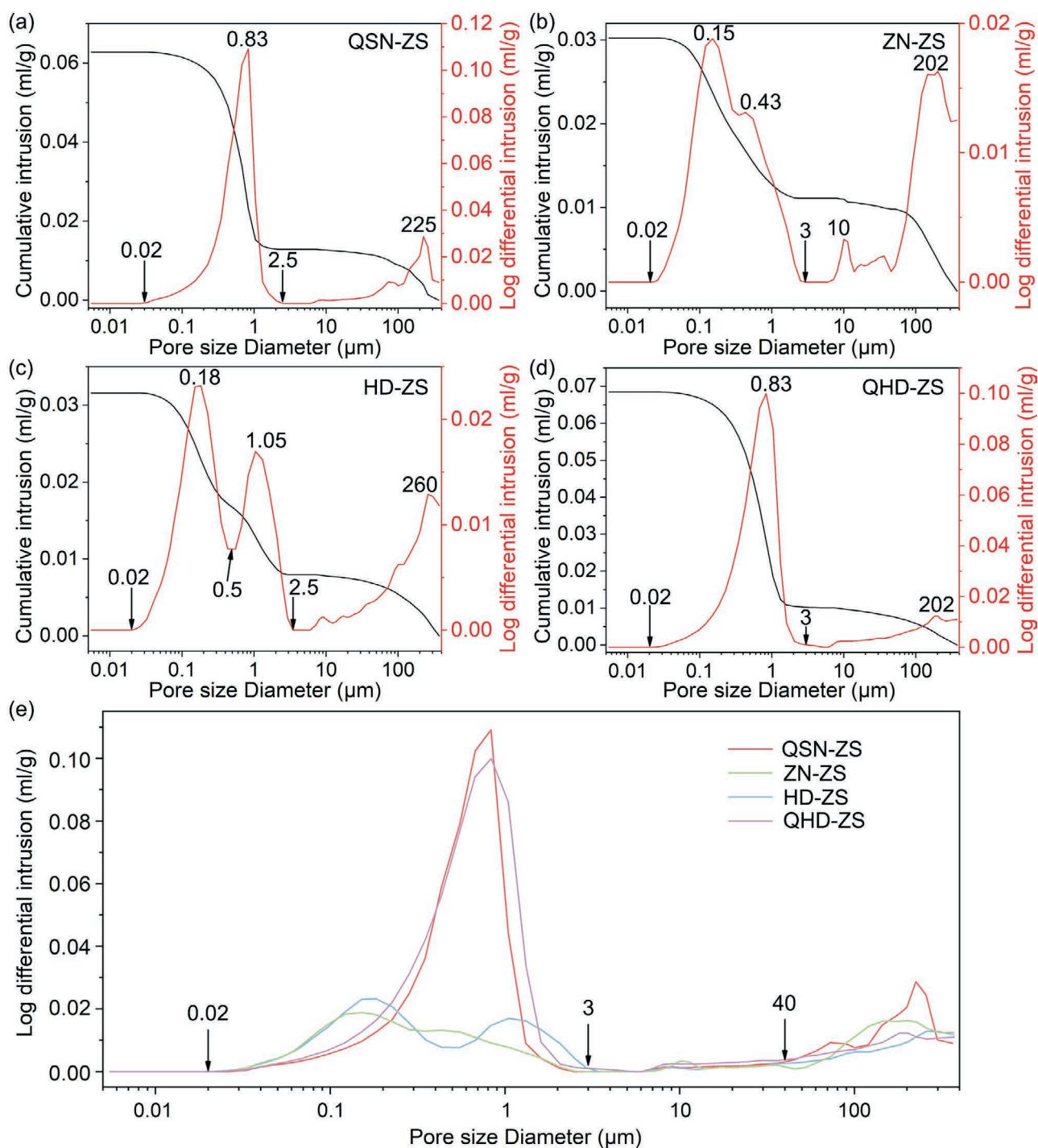


Fig. 7: Pore size distributions determined by mercury porosimetry for (a) QSN-ZS, (b) ZN-ZS, (c) HD-ZS and (d) QHD-ZS samples. (e) Comparison of pore size distribution of the four Zisha samples.

IV. Conclusions

In summary, the composition and pore structure of four Zisha clays were investigated. The main components of the four Zisha green body samples are similar, but the content varies. The ZN has the highest content of hematite among the four Zisha clays, while there is almost no hematite in the HD. All four Zisha samples have two distinct pore size distribution ranges: 0.02–3 μm and > 40 μm. The pore distribution of QSN-ZS and QHD-ZS in the range of 0.02–3 μm far exceeds that of the ZN-ZS and HD-ZS. Meanwhile, the porosity of QSN-ZS and QHD-ZS is higher than that of the other two Zisha samples. The

porosity seems to be related to the content of Fe_2O_3 , and a medium content (2.5 wt% – 5 wt%) of Fe_2O_3 is beneficial for high porosity.

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