Provenance of Zhangzhou export blue-and-white and its clay source

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ABSTRACT

Trace element compositions of 25 shards of Chinese Late Ming export blue-and-white porcelain from Zhangzhou and Jingdezhen kilns are analysed by Inductively Coupled Plasma Mass Spectrometry. Principle components analysis and REE distribution curves are used to establish method for provenance unknown Chinese export blue-and-white porcelain which may have originated from Zhangzhou or Jingdezhen kilns. By matching the REE distribution curves of Zhangzhou kiln samples and parent rocks of the possible clay sources used to make Zhangzhou blue-and-white, and comparing it with previous results of geological, geochemical and archaeological researches, the clay used for producing Zhangzhou export blue-and-white has been identified as having been collected from the weathered shells of a nearby potassium feldspar miarolitic granite outcrop.

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1. Introduction

Ceramics are especially durable and can therefore be used as one of the best indicators of ancient activity. Porcelain was invented in China and as a result the history of porcelain production and its trade is reflected by the occurrence of porcelain shards all over the world. Porcelain was first produced in Yue kilns as early as the second half of 2nd century (Li, 1998: pp. 115), and at least from the 7th century Yue kiln porcelain was already exported (Lin, 1999: pp. 3–5). Since that time onwards in a more or less uninterrupted course till today, Chinese porcelain has been shipped to East Asia, Southeast Asia, the Middle East, Europe and America. The types of export porcelain have changed through time along with the development of its production technology, from early celadon, to Qingbai (an early type of white ware with a hint of green in the glaze), to blue-and-white, and to polychrome wares (The Chinese Ceramic Society, 1982: pp. 381–385).

By the middle of the 16th century an exciting age of exploration had begun for half a century from the time when Vasco Da Gama discovered the carreira da India (sea route to India), the Portuguese had been trading with Asia for several decades and the Spanish and Dutch were also about to embark on trading activities. At the same time in China the Ming dynasty (1368–1644 AD) was officially

waning eventually leading to its downfall. However, this unstable domestic political situation provided the maritime trader with the best environment in which to export porcelain at a time when the world famous blue-and-white ware had already reached its maturity. The government had loosened its grip on official kiln production in Jingdezhen by the middle Ming period, so porcelain technology and its products spread more easily. At the time the Great Ming government was also too corrupt and internally preoccupied to hold on to the maritime trade ban that had been introduced in the Early Ming period, and with the inclusion of new traders and customers (the Europeans) the peak of Chinese porcelain exportation was imminent, and the production peak lasted for over a century (Ho, 1996). According to Volker (Volker, 1954: pp. 223–225), between 1602 and 1682 the V.O.C alone traded more than 16 million pieces of Chinese export porcelain.

Due to the demand for Chinese porcelain, and the existence of a large amount of research material, western scholar's research on Chinese export blue-and-white started very early and significant achievements have been made. Most of these researches are of an Art Historical nature using material in museum collections and from shipwreck excavations and they are generally concerned with typology (Harrisson, 1979; Pijl-Ketel, 1982; Rinaldi, 1989). However, there has been a shortage of information about the kiln sites. Before the archaeology of export porcelain had the important break-through in 1990s which discovered Zhangzhou kilns and Jingdez-hen export porcelain production remains, Chinese scholars had minimal knowledge about late Ming export blue-and-white. The research on export blue-and-white in China therefore had big

breakthroughs from the 1990s onwards and could finally be connected to research in the West.

Excavations and surveys have so far shown that there were two major export porcelain production areas in China in the late Ming dynasty, Jingdezhen and the Southeast coast: the Zhangzhou kilns were the most typical and important sites in the Southeast coast region (Fujian Museum, 1997: pp. 112–121). Generally speaking, western scholars have suggested that high and middle quality Chinese export blue-and-white, typical 'Kraak ware', were manufactured for the European market in the late Ming dynasty, and some middle and low quality export blue-and-white porcelain such as 'swatow' with kiln grit adhering to the foot were manufactured mainly for the Japanese and Southeast Asian market. They also suggested that 'Kraak ware' was made in Jingdezhen, and 'swatow' was made on the Southeast coast (Harrisson, 1979: pp. 10–14, Rinaldi, 1989: pp. 13–20). This categorization and the suggested provenance of late Ming export blue-and-white porcelain is a major contribution, and in most of cases it makes sense. However, over the last two decades it has been suggested that kiln sites in Zhangzhou could also be the origin of 'Kraak ware' (Pei, 2002: pp. 1–9), and that some kiln sites in Jingdezhen produced low quality export blue-and-white wares with kiln grit adhering to the foot as well (Cao, 2002). So these comparatively new discoveries have generated debate on the origin of a proportion of Chinese export porcelain, whether Zhangzhou or Jingdezhen kilns, or somewhere else. Examples are the octagonal dishes found in the Binh Thuan shipwreck (Christie's Australia Pty Ltd, 2004: pp. 8) and the tripod censer in Museum of East Asian Art, Bath (Jorge Welsh Oriental Porcelain & Works of Art, 2006: pp. 15). Therefore, this situation has led to a debate as to whether typology alone is a reliable and comprehensive way to provenance late Ming dynasty Chinese export porcelain. Therefore a focus of this article is to assess whether a scientific approach can resolve some of these issues relating to the provenance of Late Ming Chinese export blue-and-white porcelain.

2. The samples

Samples of Zhangzhou export blue-and-white porcelain were collected from 5 formally excavated kiln sites: (1) Hua-Zai-Lou kiln (HZ), (2) Tian-Keng kiln (TK), (3) Bei-Gou kiln (BG), (4) Da-Long kiln (DL) and (5) Er-Long kiln (RL). (1) And (2) are located in Nansheng town; (3), (4) and (5) are located in Wuzhai town. Both towns are located in Pinghe county, Zhangzhou, Fujian province, PR China

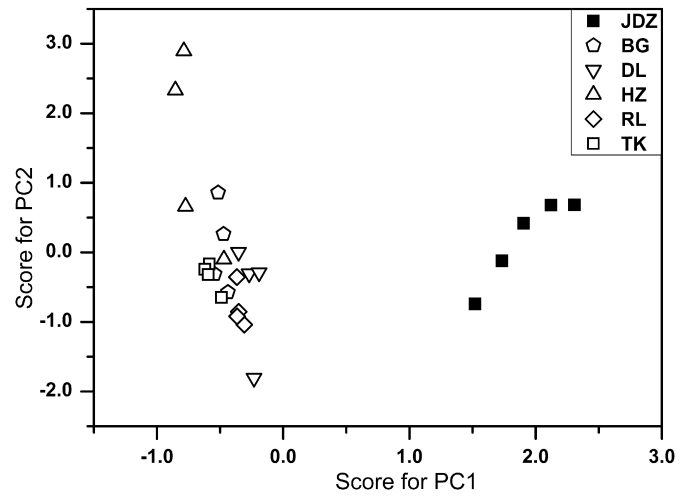Fig. 1. Variable loading plot shows elements' correlation between the first and second components.

Fig. 2. Component score plot (Jingdezhen = JDZ; Bei-Gou kiln = BG; Da-Long kiln = DL; Hua-Zai-Lou kiln = HZ; Er-Long kiln = RL; Tian-Keng kiln = TK).

(The locations of Zhangzhou and Jingdezhen about China, and the locations of Nansheng town and Wuzhai town about Zhangzhou are shown in Fig. 7).

The five formally excavated kiln sites were the Zhangzhou kilns with the finest product quality; the sites were chosen using

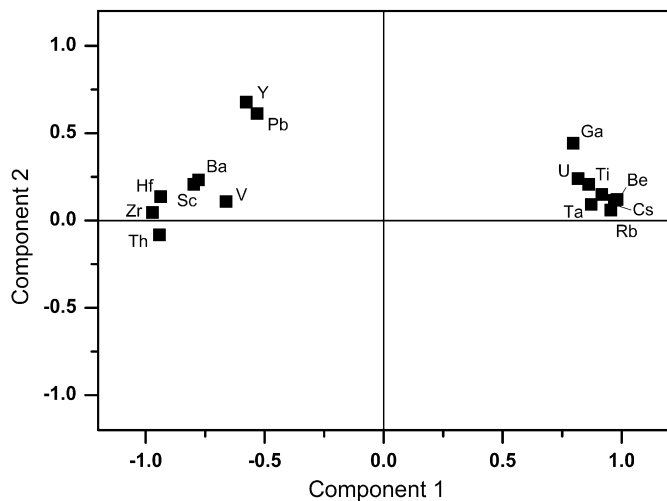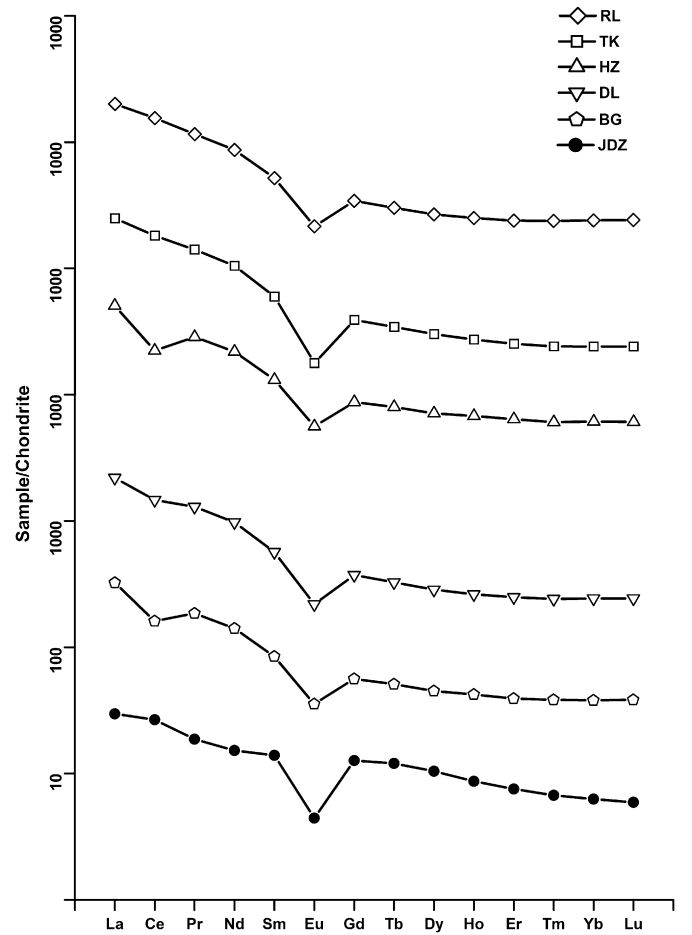Fig. 3. REE distribution curves of Zhangzhou kilns' samples and Jingdezhen's samples, elements' means of each group are used for the plot (Er-Long kiln = RL; Tian-Keng kiln = TK; Hua-Zai-Lou kiln = HZ; Da-Long kiln = DL; Bei-Gou kiln = BG; Jingdezhen = JDZ).
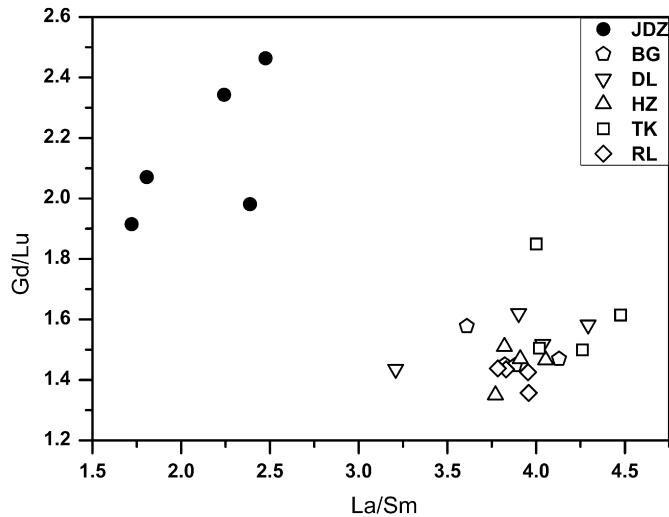
Fig. 4. Plot of La/Sm versus Gd/Lu to demonstrate the distinctions on declines from La to Sm and from Gd to Lu between Zhangzhou pattern and Jingdezhen pattern (Jingdezhen = JDZ; Bei-Gou kiln = BG; Da-Long kiln = DL; Hua-Zai-Lou kiln = HZ; Tian-Keng kiln = TK; Er-Long kiln = RL).

information from archaeological surveys. The term 'Zhangzhou kilns' has been specified to represent the kilns specializing in producing export porcelain of late Ming to early Qing dynasty and distributed across Zhangzhou County, located in the southeast corner of China in Fujian province.

Jingdezhen was a porcelain production centre since the Yuan dynasty (1206–1368 AD). Export porcelain belonged to the 'folk kiln' category in Ming dynasty. The Folk kiln, rather than an official kiln, is a kind of kiln that was run by one family or families. Its production mode was like an industrial assembly line, each production step being carried out by a specific group of workers who only focused on their own practice (Fang, 2002: pp. 3–12). In the late Ming period, Jingdezhen folk kilns were supplying products for multiple demands: official demands, domestic markets, over-seas markets, and even foreign royal family orders. This production pattern in Ming dynasty Jingdezhen folk kilns makes it highly likely that no kiln site exclusively producing export blue-and-white like Zhangzhou kilns existed in Jingdezhen, at least no such kiln site
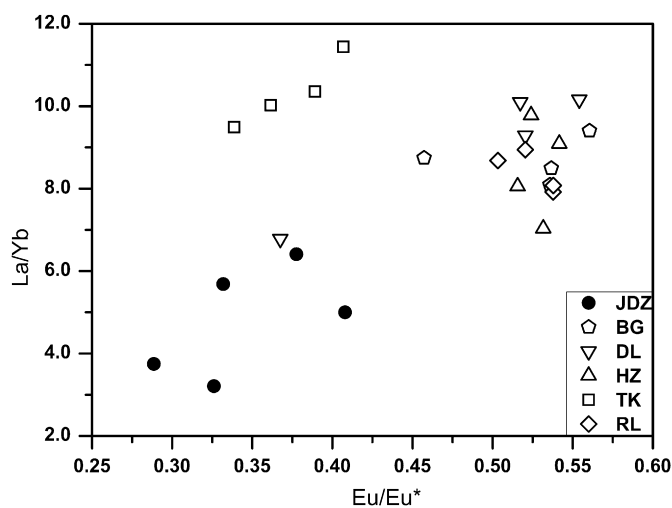

Fig. 5. Plot of Eu/Eu* versus La/Yb to demonstrate the differences on basic REE pattern profile between Zhangzhou pattern and Jingdezhen pattern (Jingdezhen = JDZ; Bei-Gou kiln = BG; Da-Long kiln = DL; Hua-Zai-Lou kiln = HZ; Tian-Keng kiln = TK; Er-Long kiln = RL).
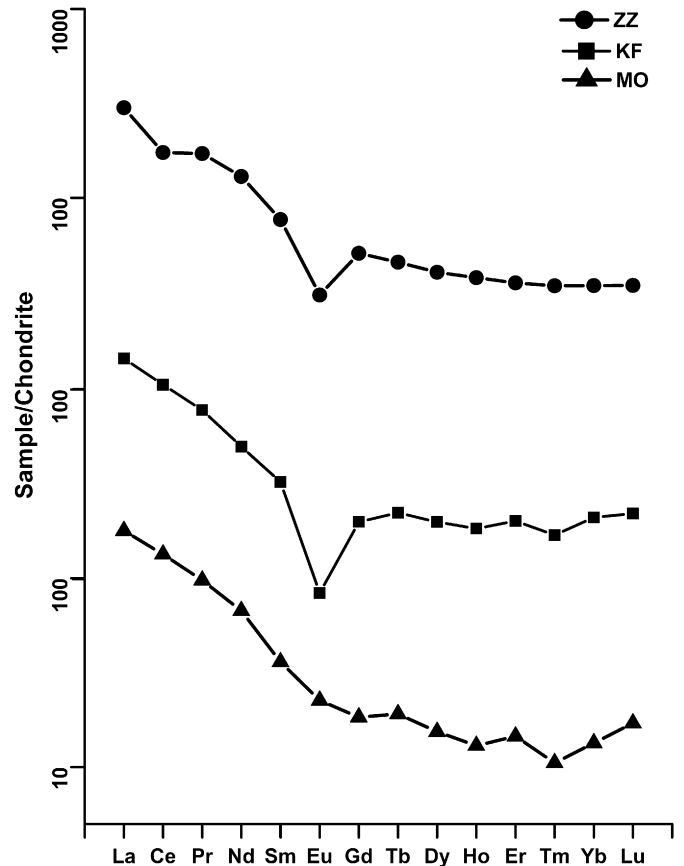

Fig. 6. REE distribution curves of Zhangzhou export blue-and-white porcelain samples, Zhangzhou K-fledspar miarolitic granite and Zhangzhou monzogranite (Zhangzhou kilns = ZZ; K-fledspar miarolitic granite = KF; monzogranite = MO).

remains have been found yet. However in the 1990s Kraak style shards were found on several late Ming kiln sites in Jingdezhen (Cao, 2002): our Jingdezhen export blue-and-white samples are collected from these sites.

3. Methodology

The methodology of provenance ceramic artefacts by grouping them according to elemental concentrations found in ceramic bodies has been established for a long time, and it has proven to be legitimate and useful (Tite, 2008). The development of increasingly accurate and sensitive analytical techniques has made this method increasingly relevant. However, because the production of porce-lain involved roughly the same raw materials, a delicate refinement procedure, and a developed production technology, when prove-nance study concerns porcelain wares, statistical analysis and grouping major elements have been found not especially adequate for accurate provenance in some cases (including the present one), so more and more research tends to focus on the use of trace elements analysis as an alternative way for provenance porcelain wares (Xie et al., 2009).

For the sake of improving analytical coherence and archaeo-logical meaning, recent provenance research has tended to involve bigger sample sets and the analysis of a wider range of elements. Because of this it has become more and more challenging for researchers to discuss each element individually or by using bi-plots, so multivariate statistics have been used. With the accumu-lation of successful case studies, and an increasingly deeper understanding of how multivariable statistics should be used
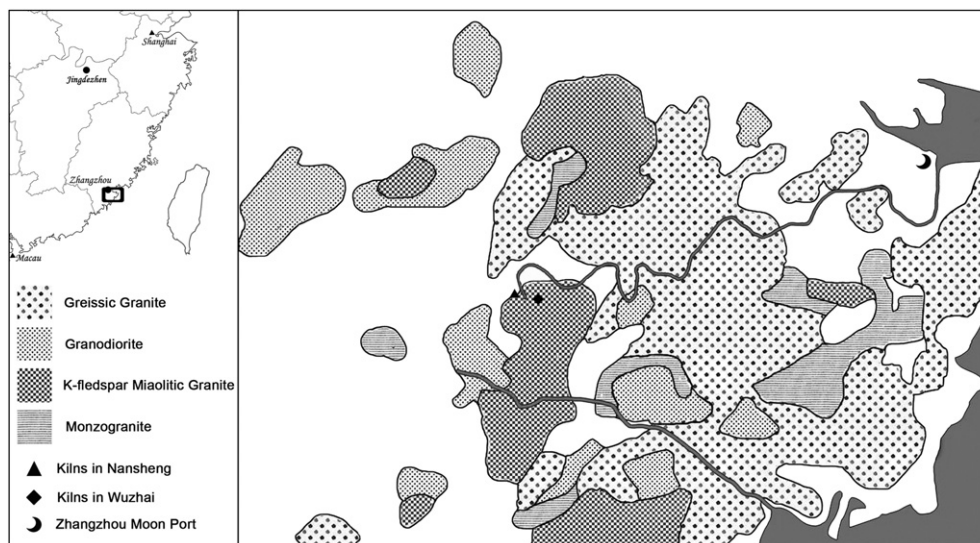
Fig. 7. The map of the relationship of Zhangzhou kilns, local rocks, the available water transportation and the moon port.

properly in provenance research, the combination of elemental analysis and multivariable statistics has developed into a more precise approach.

The determination of Rare Earth Element (REE) concentrations occupies a special position in this research area. Ceramic raw materials, such as clay, produced by different geological processes, have unique REE distribution patterns, and these are very stable and not easily changed during the ceramic production process or in burial environments (Allen et al., 1982, Bishop et al., 1982). So the attribution to group using REEs gives us a powerful tool to link raw materials to the products, and in the present research, we try to use this tool to provenance the raw materials used at the Zhangzhou kilns.

The inductively coupled plasma mass spectrometry (ICP-MS) facility employed in the present research is ELEMENTs made by FINNIGAN MAT from the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Science. The analytical conditions were as follows: 1250 W; Dual electron multiplier analogue/ion counting detection modes; Mess Resolution: 300; Sample Gas: 0.85 l/min; Auxiliary Gas: 0.83 l/min; Cool Gas: 13.5 l/min.

The sample preparation procedure used was divided into five steps:

1. To make sure that only the porcelain body was analysed, prior to pulverization, the glaze was ground off using a diamond grinding wheel and the body rinsed in an ultrasonic bath with deionised water for 30 min. Then samples were ground to a 200 mesh in an agate mill, and heated in an oven at 120° for 8 h.
2. For each sample 40 mg of powder was weighed in a Teflon reaction tube, and combined with 0.5 ml 1:1 HNO_3, 2 ml HF and oscillated in an ultrasonic bath for 15 min. Then the solution was evaporated to near-dryness. One ml HF was added to the solution, and it was evaporated to near-dryness again.
3. 0.5 ml 1:1 HNO_3, 1.5 ml HF, 1 ml $HCLO_4$ was added to the solution, kept at 200 °C oven for five days, then evaporated to near-dryness again.
4. 2 ml 1:1 HNO_3 was added to the solution, kept at 150 °C in an oven overnight and then evaporated to near-dryness again.
5. 2 ml 1:1 HNO_3 was added to the solution, kept overnight, then 40 μl HF and 1 ml 500 ppb Indium were added to the solution. Then the solution was decanted into 50 ml flasks with 1% HNO_3.

Three China national certified reference materials − GBW07104 (Andesite), GBW07105 (Basalt), GBW07107 (Shale), were measured along with the samples to monitor any variation in the results. The quality control sample is the China national certified reference material − GBW07103 (granite).

4. Results

4.1. Using trace elements to provenance Zhangzhou export porcelain

Our ICP-MS analyses determined 38 trace elements in the samples. The results of quality control sample (GBW07103) are shown in the Table 1 and suggest that the determined values are similar to the literature values. Results of analyses on archaeological samples are shown in the Table 2.

Two separate techniques were employed to present the results of non-REE trace elements and rare earth elements respectively: principle component analysis (PCA) and REE distribution patterns.

For the principle component analysis, a procedure was carried out in order to test whether the dataset was suitable to make a PCA analysis and whether some elements should be excluded from the analysis in order to make the PCA more meaningful. The objective of doing a PCA is to use less transformed variables (principle components) to replace the original variables, and retain as much original data information as possible. The data will then become easier to handle. A PCA will be informative only when there is a reasonably high degree of correlation amongst the groups of variables selected (Baxter, 1994: pp. 47–48). According to statistical theory, the more the chosen variables are correlated, the better the principle components represent the chosen group of variables, the more the original information is retained (Shennan, 1988: pp. 264–265). This means that if there are variables in the original dataset which are not closely correlated with other variables, when doing a PCA such variables should be excluded from the chosen group because not only do they not represent the basic features of the data, but also they would undermine the information from other closely correlated variables.

There are several methods to test the degree of correlation amongst variables, and the most straightforward and commonly used way is by calculating the correlation matrix of the dataset. In our case, our original dataset is a 25 × 38 (samples × elements)

Table 1
Results of quality control sample (GBW07103).

GBW07103	Li	Be	Sc	V	Cr	Co	Cu	Zn	Ga	Rb	Sr	Y	Zr
Test values	18.1	0.8	9.7	93.0	30.5	12.6	55.8	58.9	18.5	35.2	804	9.0	88.0
Literature values	18.3	1.1	9.5	95.5	32.4	13.2	55.4	71	18.1	37.6	790	9.2	99.0

GBW07103	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Tm
Test values	5.2	2.0	993	20.6	41.0	4.6	18.2	3.4	1.1	2.6	0.36	1.8	0.1
Literature values	6.8	2.3	1020	21.8	40.0	4.9	19.0	3.4	1.0	2.7	0.41	1.8	0.1

GBW07103	Yb	Lu	Hf	Ta	Pb	Th	U
Test values	0.9	0.1	2.6	0.4	9.6	2.9	0.9
Literature values	0.9	0.1	2.9	0.5	11.3	2.6	0.9

chemical composition matrix. From the calculation, 16 elements with a reasonably high degree of correlation with each other were included into our chosen group, 7 elements Cu, Zn, Co, Cr, Sr, Nb, Bi were excluded, because their average moduli of correlation coefficients are less than 0.5. Rare earth elements are excluded, due to their extremely strong correlation with each other. As a whole, they unduly influence the principal components, creating biased PCA results.

Using the correlation matrix for the standardized data of 25 samples × 16 elements to calculate the principle components, the first principle component explains 71.65% of the total variance and the second explains 8.30% of the total variance. The cumulative variance explained by first two principle components is 79.96%, which is an ideal situation for PCA.

The results from PCA are displayed as a set of bi-plots. In the variable loading plot (Fig. 1), the first and second component loadings of the elements, representing the correlation of the principle components with the elements, are used as abscissa and ordinate to mark their positions. In our case, three groups of variables – (Ba, V, Sc, Hf, Zr, Yh), (U, Ti, Li, Be, Cs, Rb, Ta, Ga) and (Y, Pb) are shown in the plot. The group that includes U, Ti, Li, Be, Cs, Rb, Ta, Ga are positively correlated with the first component; Ba, V, Sc, Hf, Zr, Yh are negatively correlated with the first component, and Y, Pb take most of the weight of the second principle component.

On the other hand, in the component score plot (Fig. 2), for the first principle component, Jingdezhen samples are located in a constrained group on the right hand side of the plot and Zhangzhou samples are distributed in a constrained group on the left hand side of the plot.

Looking Figs. 1 and 2 together can be very helpful in providing a clear understanding of the relationship between samples and elements. Generally speaking, samples located away from the origin will tend to have relatively high values for those elements that occupy the equivalent space on the variable plot (Baxter, 1994: pp. 67–69). So in our case, Jingdezhen samples have higher levels of U, Ti, Li, Be, Cs, Rb, Ta and Ga, and Zhangzhou samples have higher levels of Ba, V, Sc, Hf, Zr and Yh; the compositional differences for these elements are therefore quite significant.

The principle components are orthogonal to one another, which means the second principle component tends to exhibit information not included in the first (Shennan, 1988: pp. 265–266). In our case the first principle component mainly reflects the compositional differences between Zhangzhou samples and Jingdezhen samples for element groups of (U, Ti, Li, Be, Cs, Rb, Ta, Ga) and (Ba, V, Sc, Hf, Zr, Yh). The second principle component mainly reflects the information represented by Y and Pb which take most of the weight of the second principle component, but exclude the information that is revealed by the first principle component. In the second principle component dimension, there is no obvious displacement between the major part of Zhangzhou group and the Jingdezhen group, most dots being distributed between −1.0 and 1.0, but there is a normal distribution of Zhangzhou samples, its range covering

from 3.0 to −2.0. This distribution pattern means the compositional variation of Y and Pb within the Zhangzhou sample group is much more significant than the composition differences of Y and Pb between Zhangzhou samples and Jingdezhen samples. Therefore it is mainly a reflection of the compositional difference within Zhangzhou samples group.

Fig. 3 presents REE distribution curves for the samples. In nature, REEs normally occur as +3 ions that vary in size in a regular manner (decreasing in ionic radius with increasing atomic number, from La to Lu). Since REEs are included as trace impurities in various minerals on the basis of their size and charge, the concentrations of the REE normally show a smooth variation in concentration with size (or atomic number). In some cases, there is an 'anomaly' in the behaviour of Eu, which can be separated from the others when it is reduced partially to the +2 oxidation state, or there is a Ce anomaly in some cases, due to the diverging behaviour of +4 Ce oxidation state (Allen et al., 1989).

In order to see the geochemical effect on the distribution of these elements it is necessary to normalize the concentrations so as to eliminate the effect of cosmosynthesis on natural abundances. This is done by dividing the concentrations of each REE found in a sample by the concentration of that element found in chondritic meteorites.[1] The meteorite concentrations of the REE are thought to represent the relative elemental concentrations prior to any geochemical differentiation that separates one element from another (Rollinson, 1993: pp. 135–137).

The REE distribution curves of Zhangzhou and Jingdezhen kiln samples are shown in Fig. 3. Except for slight differences on the Ce and Eu anomalies, the five curves for Zhangzhou kilns have the same pattern and this pattern is quite distinct from the Jingdezhen pattern.

Firstly the absolute REE concentrations in Zhangzhou kiln samples are several times higher than those in Jingdezhen samples. The curves for Zhangzhou kiln samples are generally between lg50 and lg500, and the curves for Jingdezhen samples are between lg5 and lg50.

Secondly, at the low REE (LREE) end, the decline from La to Sm in the Zhangzhou pattern is higher than found in the Jingdezhen pattern, and at the high REE (HREE) end, the decline from Gd to Lu in the Zhangzhou pattern is lower than found in Jingdezhen pattern. These distinctions look even clearer when plotted as La/Sm versus Gd/Lu, as in Fig. 4.

Thirdly, the proportion of LREE to HREE in the Jingdezhen pattern is lower than in Zhangzhou pattern, and the Eu anomaly of Jingdezhen pattern is higher than that of Zhangzhou pattern, apart from the results of Tian-Keng kiln. Normally, the value of Eu/Eu*[2] is used as the parameter to display the degree of the Eu anomaly present; the value of La/Yb is used to represent the proportion of

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[1] In our research, the average of C1 chondrites (Evensen et al., 1978) has been used.

[2] Eu* is the interpolate value of Sm and Gd, Ce* is the interpolate value of La and Pr.

Table 2

38 trace element composition of 25 samples of export blue-and-white porcelain body from Jingdezhen and Zhangzhou kilns (Jingdezhen = JDZ; Bei-Gou kiln = BG; Da-Long kiln = DL; Hua-Zai-Lou kiln = HZ; Tian-Keng kiln = TK; Er-Long kiln = RL; Unit: μg/g).

	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr
JDZ1	235.9	10.7	2.2	8.5	1.9	7.7	5.3	20.0	64.0	36.4	504.9	39.3
JDZ2	368.2	8.8	2.5	3.0	2.3	2.6	5.3	8.5	516.5	30.2	320.4	69.7
JDZ3	213.3	13.8	2.7	7.4	3.5	8.2	2.9	14.0	62.1	39.4	523.4	42.7
JDZ4	127.5	10.7	1.8	6.9	2.8	11.4	6.9	17.3	75.8	28.0	389.9	37.9
JDZ6	158.5	11.3	2.9	7.1	2.9	10.3	3.4	9.5	57.1	34.3	442.6	37.6
BG1	9.8	2.5	7.2	24.2	4.7	8.2	5.9	13.5	47.0	22.9	175.2	48.7
BG2	10.0	2.7	5.8	15.5	2.7	9.6	3.9	12.6	60.8	21.0	171.0	44.5
BG8	8.2	1.8	7.9	15.9	4.2	4.5	4.2	12.0	54.2	21.1	196.3	63.8
BG10	4.8	2.5	7.2	17.9	3.6	6.5	3.0	8.3	39.9	23.1	168.9	37.8
DL3	6.2	2.0	7.0	21.6	3.7	12.1	2.8	19.0	33.7	23.2	217.1	46.5
DL5	6.8	3.1	7.4	21.9	3.3	5.0	2.9	15.7	68.9	24.5	220.3	77.8
DL7	7.2	2.4	5.8	5.5	1.7	2.1	10.5	5.1	32.0	18.2	169.3	52.3
DL8	7.1	3.4	6.5	23.6	4.6	6.0	5.6	11.1	57.8	23.8	234.4	81.1
HZ2	8.8	2.2	6.5	22.3	4.0	6.4	4.0	12.2	53.4	22.8	179.6	49.4
HZ11	8.0	2.4	8.8	13.5	2.2	5.3	3.8	16.1	68.0	28.1	152.6	30.8
HZ13	5.0	2.6	8.6	17.6	2.6	5.0	1.3	11.0	69.3	26.1	200.1	45.9
HZ20	6.3	2.0	8.5	22.3	5.9	5.6	3.8	11.2	65.3	25.0	155.1	44.9
TK1	6.2	2.4	10.9	11.2	3.5	2.2	1.5	11.8	59.5	25.8	182.3	45.7
TK5	7.8	2.3	8.0	17.8	3.8	5.3	5.0	11.4	66.8	23.5	184.8	40.6
TK6	6.0	2.4	10.5	14.5	8.0	2.0	3.2	9.1	71.7	26.0	171.1	44.4
TK10	6.2	2.4	9.4	11.1	3.4	2.7	1.5	9.3	74.3	25.2	178.1	47.6
RL4	5.3	2.2	4.2	13.3	1.9	6.2	3.5	9.0	32.4	19.5	225.6	48.9
RL5	4.5	2.1	4.3	14.2	3.1	4.8	4.5	9.9	57.0	21.3	223.3	46.8
RL12	4.1	2.2	4.6	14.3	3.2	4.6	4.0	8.0	66.3	21.0	215.7	47.3
RL16	3.1	2.3	4.9	14.3	4.1	7.5	4.2	7.9	57.5	20.9	201.7	38.3

	Y	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
JDZ1	12.6	52.6	21.6	56.9	160.8	4.2	13.9	1.1	4.8	1.5	0.2	1.9	0.3
JDZ2	18.7	43.5	37.8	68.8	356.8	11.2	14.4	2.7	10.5	3.1	0.4	3.7	0.6
JDZ3	18.4	51.6	23.7	65.3	148.2	6.6	15.3	1.7	7.3	2.3	0.2	2.9	0.5
JDZ4	7.8	53.7	18.4	43.6	127.2	4.9	18.3	1.2	4.4	1.2	0.2	1.5	0.2
JDZ6	16.0	57.7	20.7	55.7	221.8	8.2	19.8	2.0	7.7	2.1	0.3	2.6	0.4
BG1	59.6	187.7	24.3	4.8	652.7	77.3	107.9	17.6	65.9	12.6	2.0	11.1	1.8
BG2	53.4	167.3	25.8	4.8	408.9	64.3	96.2	15.5	58.4	11.1	1.5	9.8	1.6
BG8	51.7	156.3	22.8	4.4	847.5	67.3	92.3	14.7	54.0	10.2	1.7	9.0	1.4
BG10	90.2	155.2	25.5	5.3	442.9	105.5	101.5	22.4	84.8	17.0	2.8	15.9	2.6
DL3	41.5	145.2	26.3	4.8	509.4	56.7	98.9	12.9	48.1	8.8	1.4	7.7	1.2
DL5	39.6	161.9	25.0	4.9	665.2	56.2	106.9	12.3	45.0	8.2	1.4	7.3	1.1
DL7	41.1	114.6	30.5	3.5	192.6	42.3	57.5	10.5	40.2	8.2	0.9	7.4	1.3
DL8	34.1	150.8	24.3	5.3	684.7	52.7	96.6	12.3	45.6	8.4	1.3	7.2	1.1
HZ2	55.1	169.4	24.7	4.8	546.7	65.7	103.1	15.1	55.8	10.5	1.7	10.0	1.7
HZ11	155.4	178.5	29.2	2.8	651.8	155.7	132.4	34.0	128.7	25.8	4.4	24.9	4.3
HZ13	120.5	171.3	22.5	3.8	898.3	168.3	152.7	36.9	141.3	27.5	4.4	23.2	3.8
HZ20	53.5	171.1	20.3	3.9	888.5	89.0	157.6	20.0	73.5	13.7	2.1	11.3	1.7
TK1	40.4	165.0	19.8	5.3	619.4	61.1	111.3	13.1	47.1	8.5	1.0	7.9	1.3
TK5	42.1	160.8	16.8	5.8	489.9	70.6	106.8	16.0	59.5	11.0	1.3	9.6	1.5
TK6	34.1	168.3	19.5	5.1	605.2	54.1	113.2	11.9	43.5	7.9	0.9	6.9	1.1
TK10	33.1	166.9	20.3	5.2	627.4	50.7	114.4	11.4	41.7	7.9	0.8	6.8	1.1
RL4	47.8	156.6	24.8	4.6	622.1	55.8	85.0	12.6	47.2	9.1	1.5	8.5	1.4
RL5	32.9	164.2	26.8	4.4	629.6	44.8	95.1	9.9	35.0	7.1	1.1	6.1	1.0
RL12	33.6	161.9	26.8	4.1	633.1	42.5	92.4	9.6	35.8	6.7	1.1	6.1	1.0
RL16	34.2	158.2	26.4	4.8	581.8	47.1	107.6	10.8	40.4	7.8	1.2	6.6	1.0

	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U
JDZ1	2.1	0.4	1.0	0.1	0.9	0.1	3.4	6.1	2.6	38.1	0.0	5.7	10.9
JDZ2	3.6	0.6	1.5	0.2	1.3	0.2	4.0	10.1	1.7	40.2	0.2	6.2	10.3
JDZ3	3.1	0.6	1.5	0.2	1.2	0.2	3.5	6.3	2.6	29.8	0.0	8.0	11.5
JDZ4	1.4	0.3	0.7	0.1	0.5	0.1	3.3	4.0	2.0	39.3	0.0	5.8	8.2
JDZ6	2.7	0.5	1.3	0.2	1.1	0.2	3.4	5.0	2.1	34.3	0.1	7.0	8.1
BG1	10.7	2.2	6.0	0.9	6.2	0.9	6.6	2.2	1.4	34.8	0.0	29.8	6.8
BG2	9.6	2.0	5.2	0.8	5.0	0.8	6.4	2.4	1.3	59.9	0.0	28.3	6.0
BG8	8.8	1.8	5.0	0.8	4.9	0.8	5.6	2.1	1.5	34.6	0.0	30.7	6.6
BG10	16.2	3.3	9.1	1.4	8.9	1.4	5.8	2.5	1.3	55.6	0.0	33.4	6.4
DL3	7.3	1.5	4.1	0.6	4.1	0.6	5.5	2.5	1.6	42.8	0.0	32.3	7.2
DL5	6.8	1.4	3.8	0.6	3.8	0.6	5.9	2.1	1.3	44.5	0.0	27.3	7.7
DL7	7.7	1.6	4.4	0.6	4.2	0.6	5.5	3.3	1.0	40.2	0.0	38.6	4.8
DL8	6.3	1.3	3.7	0.5	3.5	0.6	5.7	2.2	1.6	37.9	0.0	29.9	9.1
HZ2	9.8	2.1	5.8	0.8	5.5	0.8	6.4	2.3	1.4	43.6	0.0	30.7	6.8
HZ11	27.1	5.7	15.8	2.3	15.0	2.3	7.8	2.4	1.2	54.6	0.0	32.3	5.0
HZ13	22.7	4.8	13.1	1.9	12.6	1.9	7.0	1.9	1.6	68.9	0.0	32.3	7.1
HZ20	10.2	2.2	6.1	0.9	6.2	1.0	6.9	1.7	1.3	51.4	0.0	28.9	5.4
TK1	7.7	1.6	4.2	0.6	4.0	0.6	6.8	1.7	1.3	45.0	0.1	27.7	4.1
TK5	8.8	1.7	4.5	0.6	4.2	0.6	6.5	1.6	1.4	41.2	0.0	27.0	4.2
TK6	6.8	1.4	3.8	0.6	3.7	0.6	7.1	1.7	1.3	44.3	2.2	29.3	4.1

Table 2 (*continued*)

	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U
TK10	6.5	1.3	3.7	0.6	3.6	0.6	7.3	1.8	1.2	45.8	0.2	30.5	4.5
RL4	8.2	1.8	4.8	0.7	4.8	0.7	6.2	2.5	1.4	37.7	0.0	29.4	5.5
RL5	5.7	1.2	3.4	0.5	3.4	0.5	6.5	2.6	1.5	43.1	0.0	30.0	5.0
RL12	6.1	1.2	3.5	0.5	3.6	0.6	6.5	2.6	1.2	42.1	0.0	28.3	5.8
RL16	6.3	1.3	3.6	0.6	3.7	0.6	6.4	2.7	1.6	51.4	0.0	32.5	5.6

LREE to HREE. These two parameters are usually put together to demonstrate the basic profile of one REE distribution (Li et al., 2003). In our case, the basic profile differences between Zhangzhou and Jingdezhen patterns look clearer when plotted as Eu/Eu* versus La/Yb as in Fig. 5.

Although the REE pattern shared by five Zhangzhou kiln samples is significant, there are two minor differences between them. These are the presence of a bigger Ce anomaly in the Bei-Gou and Hua-Zai-Lou curves, and a bigger Eu anomaly in the Tian-Keng curve. As discussed below, the Ce and Eu anomalies are two important parameters for that reflect the degree of weathering of the clay. Although the clay used for the different Zhangzhou kilns was probably were from the same geological source, it is highly likely that the potters from different kilns collected their clay from slightly different locations with slightly different weathering resulting in the small differences in Ce and Eu anomalies between the different Zhangzhou kiln REE patterns. This is also the reason why the dots representing Tian-Keng samples in Fig. 5 separate from other Zhangzhou samples, forming another group.

In Fig. 5 there is an outlier from Da-Long samples located in the area that is typical of Jingdezhen samples. The existence of this outlier does not undermine the method of using REE distribution patterns to distinguish Zhangzhou samples and Jingdezhen samples, because Fig. 5 only reflects one aspect of the differences between REE patterns between Zhangzhou and Jingdezhen samples. Although there is an outlier, when all criteria are combined, still this method is able to identify which group it should belong to.

As demonstrated above, the geochemical information relating to Zhangzhou kilns and Jingdezhen porcelain bodies can be distinguished one from another by using both PCA and REE distribution patterns. Therefore, when there are doubts about the origin of certain late Ming Dynasty Chinese export blue-and-white wares, these two methods could be used to identify if the wares in question were produced in Jingdezhen or Zhangzhou or neither of them.

4.2. Using REE distribution patterns to provenance the clay source used to make Zhangzhou export porcelain

Generally speaking, ancient pottery kilns would have been built close to the source of clay. However, unlike Jingdezhen's detailed documentation of the sources of its porcelain production raw materials, we are unable to get any tangible information about where the old Zhangzhou potters might have collected their clay: (1) there is no historical record of the location where old Zhangzhou potters collected their clay; (2) the Archaeological excavation of Zhangzhou kilns did not provide this piece of information either; (3) there is no contemporary porcelain industry in this area. So in this case, in order to unravel the mystery of the clay source for Zhangzhou kilns, an approach involving results from geological survey and geochemical data for rocks has been adopted. Given geologists can use REE patterns to provenance the parent igneous rock of a clay sediment (Mclennan, 1989), and there is no obvious alternation of REE composition in the ceramics during firing (Kilikoglou et al., 1988) and clay refinement in production merely tends to produce a REE dilution effect on the ceramic bodies

(Allen et al., 1989), it is theoretically legitimate to adopt this method to provenance the clay that ceramics were made from.

Zhangzhou is located in southeast Fujian province near the coast at 117°−118°E and 23.5°−25°N. Its climate is controlled by the subtropical monsoon with an average rainfall per year of more than 1000 mm. Zhangzhou's geographical and climatic setting therefore provides ideal conditions for the rocks to be transformed into sediments by weathering. From the 1:500,000 geological atlas of Fujian province and other related research (Hong, 1987: pp. 1−91 Zhou, 1994: pp. 70−88), in the vicinity of Zhangzhou kilns there are four types of igneous rocks, they are Cretaceous formed K-feldspar miarolitic granite, monzogranite, granodiorite, and Jurassic gneissic granite. Su (2006) has reported that there are two types of the Kaolinitic clay deposits in Zhangzhou: weathered sedimentary Kaolin deposits weathered either from K-feldspar miarolitic granite (KF) or from monzogranite (MO). The distribution of these clays were not, however specified by Su. Therefore the aims here are to decide which clay source was used by the old Zhangzhou potters, and to try to locate them.

With the degradation of primary minerals and the development of weathered products in the process of rock weathering, because minerals have divergent degradation rates and differential leaching and elemental fixation rates, the behaviours of chemical elements exhibit significant differences in their mobilization. Because REEs have low solubility and very similar chemical properties, they are considered to be quite stable during rock weathering. However some minor fractionations do occur. From previous geological research, we know that they are predicable and follow several simple trends. As the intensity of weathering increases, the total REE abundances in the weathered product increases, the intensity of the negative Ce anomaly increases, and the depletion of high REE compared to low REE increases. At the same time the intensity of the negative Eu anomaly decreases (Cullers et al., 1987; Malpas et al., 2001; Nesbitt, 1979).

The whole-rock REE composition data of Zhangzhou K-feldspar miarolitic granite and monzogranite are taken from Zhou (1994: pp. 70−71) and Qiu et al. (2000). The REE distribution curves of K-feldspar miarolitic granite, monzogranite and Zhangzhou kiln export blue-and-white porcelain samples (the average of all the Zhangzhou samples) are plotted in the Fig. 6. At first glance, the K-feldspar miarolitic granite pattern agrees with that of Zhangzhou very well except for several minor differences, where as the monzogranite pattern is quite different from the Zhangzhou pattern. So the K-feldspar pattern was chosen to make a closer comparison with the Zhangzhou pattern in order to see if the differences could be explained by REE fractionation during rock weathering. In the event REE fractionation during rock weathering was found to be the explanation.

Firstly, the major differences between the Zhangzhou pattern and K-feldspar miarolitic granite pattern are that the Zhangzhou pattern has a bigger Ce negative anomaly and a smaller Eu negative anomaly. As pointed out by Malpas et al. (2001), when the degree of weathering increases, with the degradation and leaching of primary minerals like plagioclase and K-feldspar, the intensity of negative Ce anomaly will increase while the intensity of negative Eu anomaly will decrease in the weathered product. Therefore, the

differences of Ce and Eu anomalies between Zhangzhou and KF samples should be attributed to the REE fractionation during the clay formation processes.

Secondly, the obvious depletion of Gd–Lu in Zhangzhou samples compared with the K-feldspar miarolitic granite pattern can be attributed to the HREE depletion, which commonly occurs during rock weathering. This phenomenon, which is due to the degradation and leaching of heavy minerals in which HREE compositions are much higher than LREE, has been discussed in detail by Cullers et al. (1987) and Nesbitt (1979).

Thirdly, the difference in the total REE abundances between Zhangzhou and K-feldspar miarolitic granite samples should be caused by the de-quartz effect in weathering and clay refinement.

During weathering and clay refinement, the coarse grain non-plastic inclusions which are mostly quartz tend to be removed. Because the total REE composition borne in quartz is very low, the presence of quartz in rock or clay has a diluting effect on the total REE concentration, so when the quartz composition is decreased by weathering and clay refinement, the total REE concentration will rise, but it will not have an obvious influence on REE pattern (Allen et al., 1989).

By using previous geological research on rock weathering, the basic differences between REE patterns in Zhangzhou kiln porcelain samples and Zhangzhou K-feldspar miarolitic granite can be explained. In addition, the weathered sedimentary Kaolinitic clay weathered from K-feldspar miarolitic granite could be identified as the clay source used for Zhangzhou export blue-and-white. However, this does not enable one to pinpoint the exact place where the old Zhangzhou potters obtained their clays, because this method does not reflect the actual clay deposits and does not enable a link between the rock and the clay which may be formed from it. It has therefore not been shown to be a secure enough approach to answer the key research question. However, at least this provides us with a starting point on which to build.

5. Discussion

If we combine the tentative results above with the evidence from archaeological excavations, the historical background, and the geographical setting (Fig. 7), we find that it makes our attempt to trace the source of clay even more relative.

The development of Zhangzhou kilns has sometimes been discussed as a relatively sudden and isolated event because they functioned for only about 100 years, and there was no porcelain making tradition before or after this period in the area. But how could production on such a large scale with a wide range of vessel types and a mature technological development occur in such a relatively short period of time?

In the mid Ming dynasty, when the Great Ming government's maritime trade ban was still in force, when all the former famous ports had to cease their transactions, the Zhangzhou Moon port gradually became the most important smuggling harbour in China. When the Great Ming government started to reopen maritime trade, the Moon port was first officially opened as a trial, in 1567 AD, and the government established an office there to authorise trade licences for ships and to tax them (Li, 2001: pp. 1–5). Therefore scholars have argued that the Moon port was the primary reason for the development of the Zhangzhou kilns (Fujian Museum, 1997: pp. 112–121).

The raw material source was a primary reason why a kiln site was established. From this picture, we can see that the Zhangzhou kilns are located exactly on the edge of *Baishishan* (White Stone Mountain) K-feldspar miarolitic granite outcrop. So the potters could have collected clay from weathered shell of this outcrop for pottery production. According to the report about the clay weathered from this type of rock, the author describes the clay as a shallow deposit, with a high alumina content and low levels of iron and titanium (Su, 2006). A clay deposit like this would have been an ideal material for potting because it was easy to obtain and would have been relatively easy to wash to workable whiteness for production.

The third reason for the location of the Zhangzhou kilns has been mentioned by other scholars: the *Jiulong* (Nine Dragon) River flows close to the Zhangzhou kilns. It provided the Zhangzhou kiln sites with the safest and cheapest way to transport their products to the Moon port (Fujian Museum, 1997: pp. 112–121). There is another river several miles south of the Zhangzhou kilns leading to another port. Although it is not as famous as Moon port, it may have provided Zhangzhou potters with an alternative way to transport their products. Moreover, water from the *Jiulong* River was also very important for Zhangzhou kilns' production, since porcelain production requires large amount of water to refine the raw material. Irrespective of whether Zhangzhou potters had water powered pestles like at Jingdezhen, they still needed water to wash the clay to remove the impurities.

When we combine these three factors in relation to the map, we can understand why the Zhangzhou kilns were located where they were: their location is the nearest spot to the Moon port where there was suitable access to raw materials and to river transport.

The actual shape of Zhangzhou kilns also gives us clues about what kind of people were actually running and working the Zhangzhou kilns. The Zhangzhou kilns adopted the 'horizontal step kiln' which was a common shape for the kilns in Fujian province at that time. It is an indicator that the technology used in Zhangzhou kilns was developed within Fujian province (Fujian Museum, 1997: pp. 112–121). Therefore some scholars have argued that it was local people who were running the Zhangzhou kilns. Perhaps they did not originate from the immediate area and if not it is likely they migrated from adjacent porcelain production sites where production had been affected by the maritime trade ban.

So taking everything into account, we can be quite sure that the development of the Zhangzhou kilns was not a sudden and isolated event in history, but it was closely connected to the historical and economic background of the time. Zhangzhou kilns must have been built with a very careful design, by specialized porcelain experts, at a time when they felt the need to build a new low-cost workshop near a suitable trading centre.

When the Qing government, the successor of Ming government, held a steady dominion over the entire area of China by the last decades of 17th century, it lifted the maritime trade ban in force during its war against Coxinga (1662–1683) – the remnants of Ming dynasty based on Taiwan, and adopted an opener mind about maritime trade than the Ming government, so the ports that flourished before the Moon port regained their prosperity. But the Moon port was harmed most by the maritime trade ban and never recovered from it and soon vanished into history. The Zhangzhou kilns also ceased production and were soon abandoned as well.

6. Conclusion

A distinction between late Ming dynasty Chinese export blue-and-white porcelain wares made at Zhangzhou and Jingdezhen kilns can be made by using a combination of PCA and REE distribution patterns of trace elements.

By comparing the REE patterns of Zhangzhou kiln products with the REE patterns of the two possible parent rocks linked to the clay used by Zhangzhou kilns and relating this to geographical, historical, and economic considerations, we can suggest that the clay used by old Zhangzhou potters is from the nearby K-feldspar miarolitic outcrop containing weathered shell.

Acknowledgements

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