Compositional Characterization of Zisha clay from the Yixing area (Jiangsu, China) by Neutron Activation Analysis

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Abstract

Zisha stoneware is a distinctive pottery tradition unique to China. This ceramic tradition was highly popularized during the Ming Dynasty (AD 1368-1644), and continues to be manufactured through the present day. Throughout history, Zisha stoneware vessels have been highly desirable objects used mainly by high status individuals, and by the early 17th century was exported to Europe as trade items. Soon thereafter, European imitations of Zisha stonewares were produced in the Netherlands at Delft, and in England and Germany. Today, authentic Zisha wares are difficult to discern from imitations using the naked eye alone, which poses problems for provenance, authenticity of antiquities, and reconstructing ancient ceramic technologies developed in China. The goal of this study was to determine the elemental and mineralogical properties of Zisha clays and to evaluate their suitability for archaeological provenance study. This study used petrographic thin-section analysis and neutron activation analysis (NAA) to characterize multiple distinct types of Zisha clays, as well as other regional clays, from deposits around Huanglong Mountain (Yixing City, China). Representative samples of each clay type were sub-divided into untreated raw clays and processed and fired ceramics for comparison. The results show clays from

each major collection area have unique compositional signatures based on their trace element chemistries and mineralogical properties. Additionally, those characteristics are stable and not significantly altered by preparation or firing processes. We propose that Zisha clays have high potential for archaeological provenance studies of Zisha stoneware antiquities.

Keywords: Zisha stoneware, clay, neutron activation analysis, provenance, Yixing, China

1 Introduction

Zisha stoneware, also known as Yixing ware, purple-sand stoneware, or red stoneware, is produced using a unique type of clay found to the southwest of Yixing City, Jiangsu province (China). A regional map is shown in Figure 1. Yixing wares are considered to be highly crafted handiwork, with the most common vessel forms being Zisha tea pots. During the Ming Dynasty (AD 1368-1644), this specialized ceramic type increased in popularity to the extent that it replaced many other types of ceramic production as the preferred ware [1]. The most exquisite examples are valued as works of art among high status societies [2]. With this rise in popularity, imitations of Zisha wares began to be produced in Holland, England, and Germany in the early 17th century, and were circulated to many regions as global trade network intensified worldwide [3]. Today, Zisha stoneware maintains popularity as a high-quality ceramic type, touted as promoting health benefits related to tea infusions and low volatile compounds [4,5].

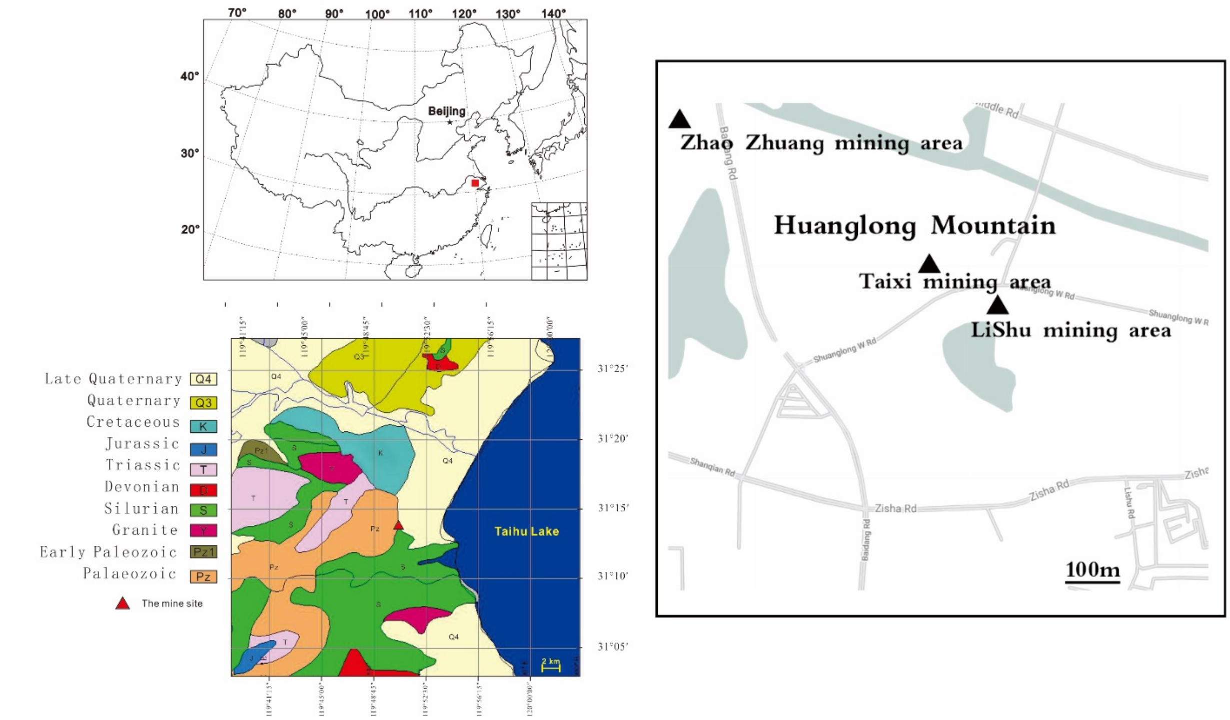

Fig. 1. Map of Yixing region and sampling sites.

In this paper, we present the trace element results from neutron activation analysis for Zisha clay from different mining areas. In general, clays were collected from the Taixi mining area, where Zisha clays originate, as well as three other locations around Huanglong Mountain. Ancient potters treated Zisha clay as the sole ingredient for making ceramic wares, as no temper or inclusions were added into the paste throughout its manufacturing history. The remaining factors we considered that might affect the trace element result composition were traditional manufacturing and firing processes. Therefore, each clay sample was divided into two parts: one part was raw materials without any processing and the other part was after processing by traditional methods and firing. A comparison of the final results shows that Zisha clays have unique chemical compositions that are highly stable and are not significantly altered by processing or firing procedures. This information is useful for future studies aimed at determining the origin and authenticity of Zisha stoneware style ceramics.

1.1 Background and Geological Context

The raw clays from Yixing occur as distinct deposits and are composed of reddish-purple sediment created by the erosion of Devonian-age (350 mya) lacustrine sediment bed. Silty mudstone is the dominant lithology and the distinctive Zisha clays are extracted from tabular or stratiform lenses between sedimentary rocks and other clay layers deep in the mineral deposits of Huanglong Mountain. The deposits appear in distinctive lenses of red, purple, and green clays, collectively referred to as purple or Zisha clay. The clay has desirable properties for ceramic production, including high plasticity and strength, low mineral inclusions, low water content, and minimal shrinkage rate. It is a homogeneous and high purity clay that can be made into ceramics with little need for processing or added mineral temper. After centuries of extensive mining activities, Yixing's Zisha clay sources have been gradually depleted [6]. In 2005, the China Yixing Municipal Government issued legislation to limit the quantity of raw materials extracted from the deposit to protect the source from further depletion.

Previous studies that compared the clays from Yixing to other regional clay deposits using XRF and SEM-EDS indicated that the clays are not distinguishable by the visual characteristics or major elemental compositions [7,8,9]. Mineral phases identified in the regional clays were also similar with Zisha clays, even after high temperature firing, showing only quartz (SiO_2) and mullite ($3Al_2O_3 2SiO_2$) [10,11]. Therefore, it is problematic to differentiate authentic Zisha wares from imitations that were produced using non-Zisha clay sources without using higher-resolution methods for trace element analysis. In archaeological studies of pottery, trace element characterization by neutron activation analysis has played an important role in addressing ceramic provenance, and the identification of workshops or production technologies [12]. This application also bears relevance for heritage science applications in which differentiating between imitation and authentic wares is important for museum collections [13].

1.2 Archaeological Prevalence

Only a small number of Yixing Zisha stoneware vessels have been recovered from archaeological excavations in China since 1959. Most high-quality examples are found in mortuary contexts such as large tombs, or are in the possession of antiquities collectors. As a result, the majority of information available about the early production of Zisha wares relies on historical literature [5]. Recently, archaeologists discovered a kiln site located in the south-east vicinity of Huanglong Mountain, which is thought to represent a production area for Zisha wares. Archaeological evidence shows that during the late Ming to Qing dynasties (16^{th}-19^{th} C.) craftspeople built kilns in the area as Zisha stoneware production intensified [14,15,16]. This tradition continues today as an important local industry. An antique Zisha stoneware is shown in Figure 2.

Fig.2. Picture of antique Zisha stoneware

2 Methods

The goal of this analysis was to determine the elemental composition(s) of unprocessed and processed and fired Zisha clays, as well as signatures of other regional clays. By establishing the characteristic geochemical fingerprints of Zisha clays, this enables future studies to determine if specific Zisha stoneware vessels were produced in the area of Huanglong Mountain, or if they could be non-local imitations.

2.1 Sample Collection and Preparation

Twenty-nine clay samples were collected from ten discrete deposits located within 2.5 square km vicinity around the Huanglong Mountain mining district. The survey focused on samples from the Taixi area, which contains the largest known deposits of Zisha clays. The survey also included other clays from other locations including Zhao Zhuang, LiShu, and Huanglong for comparison. Photographs for some of the clays are shown in Figure 3. Two samples of sherd fragments found near a kiln were also collected.

Fig. 3. The part of clay samples picture in this study: left clay is Red clay, center is green clay and right is Purple clay from Taixi

Table 1 describes the sampling locations and clay characteristics. Clays from each location were sub-sampled to analyze by neutron activation analysis (NAA) in raw and processed form. Lumped, unprocessed clays were permitted to air dry with no additional preparation. Processed clay samples were formed and stacked in open air to dry. Once dried to a suitable level, impurities were removed by hand using grinding and sieving. Once the clays were refined, small forms were hand-molded and kiln fired to a maximum temperature of 1200°C. The collection of 29 clays and two sherds were characterized by NAA, and sub-samples of clays were selected for petrographic analysis.

Table 1: Summary of sampling locations and clay characteristics.

Clay Type	Sampling Location	Lithology	Sample Preparation	ANID
Red Clay	Zhao Zhuang mining area	Mudstone; soft, light-yellow sandstones, pelitic texture and dense massive texture.	unprocessed	yxh-1
			processed and fired	yxh-2
	Huanglong mining area	Mudstone; firm light bluish-yellow ores with dense, massive texture, small muscovite mica inclusions	unprocessed	yxh-3
			processed and fired	yxh-4
	Taixi mining area - Hongpilong	Mudstone; yellow color, dense massive texture or crumb structure, small amount of small mica inclusions	unprocessed	yxh-5
			processed and fired	yxh-6 yxh-7
Tuan Clay	Taixi mining area	Muddy siltstone; very weak with rust red surface color.	unprocessed	yxz-1
			processed and fired	yxz-2 yxz-3
Purple Clay	Taixi mining area - Neng ni	Muddy siltstone; firm, brownish-purple hue; homogenous and dense structure with mica inclusions. Some ores contain thin laminates of light grey clay.	unprocessed	yxz-4
			processed and fired	yxz-5 yxz-6 yxz-7
	Taixi mining area - Hongzong (red brown)	Muddy siltstone; firm, reddish-brown, dense massive texture with mica inclusions. Traces of yellowish green pisolites with rust-red mottled surfaces.	unprocessed	yxz-8
			processed and fired	yxz-9 yxz-10 yxz-11
	Taixi mining area Dicaoqing	Muddy siltstone; firm brownish-purple with dense massive texture and small mica inclusions.	unprocessed	yxz-12
			processed and fired (fired with ash)	yxz-13
			processed and fired	yxz-14 yxz-15
	Taixi mining area Purple clay	Muddy siltstone; firm brownish-purple ores with dense massive texture, small mica inclusions. Some ores contain bedding features and mottled with spots.	unprocessed	yxz-16
			processed and fired	yxz-17
			unprocessed	yxz-18
	LiShu mining area - Tianqing	Muddy siltstone; firm, reddish ores, dense massive texture, few mica inclusions.	unprocessed	yxl-1
			processed and fired	yxl-2

		Ores exhibit conchoidal fractures when struck. Some white waxy gloss.		
Green Clay	Taixi mining area	Silty mudstone; pale light green, dense massive texture	unprocessed	yxl-4
			processed and fired	yxl-5
Sherds	Taixi mining area	Two possible Zisha type sherds; collected near a kiln	clean the surfaces, ground into powder	yxl-3 yxl-6

2.2 Neutron Activation Analysis

Elemental characterization by NAA was performed at the Archaeometry Laboratory at University of Missouri Research Reactor using procedures described in detail elsewhere [17]. Fragments of about 1cm^2 were removed from each sample and abraded using a silicon carbide burr in order to remove all potential surface contamination. The specimens were washed in deionized water and allowed to dry in the laboratory. Once dry, the individual samples were ground to powder in an agate mortar to homogenize the samples. Two analytical samples of each of the clay and ceramic powders were prepared by individually weighing 150 mg into high-density polyvials and 200 mg into high purity quartz vials. Standards of SRM-1633b Coal Fly Ash and SRM-688 Basalt Rock, and quality control samples from SRM-278 Obsidian Rock and Ohio Red Clay were similarly prepared.

The samples in polyvials were irradiated for five seconds by a neutron flux of 8 x 10^{13} cm^{-2} s^{-1}, allowed to decay for 25 minutes, at which point were counted for 720 seconds using a high-purity germanium gamma ray detector. The 720-second count yields gamma spectra containing peaks for nine elements that produce short-lived radioisotopes: Al, Ba, Ca, Dy, K, Mn, Na, Ti, and V. The samples encapsulated in quartz vials were irradiated for 24 hours at a neutron flux of 5 x 10^{13} cm^{-2} $s^{-1}$and counted twice to collect data on elements that produce mid- and long-lived radioisotopes. After 7-10 days, the first 1800 second count yields data on the following: As, La, Lu, Nd, Sm, U, and Yb. After an additional two weeks, final count of 8,500 seconds is carried out on each sample to collect data on the long-lived elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Zn, and Zr. The element concentration data from the three measurements are tabulated in parts per million. Element concentration data are provided in SI Table 1.

2.3 Petrographic Analysis

Thin sections were prepared from clay specimens that were hardened in epoxy resin, and cut and polished in cross-section. All thin sections were cut perpendicular to the surface to evaluate structural characteristics of the clay fabric. Optical analysis was performed using an Olympus polarizing microscope (BX-51) and Nikon stereoscopic microscope (SMZ1100).

3 Analytical Results

3.1 Neutron activation analysis

Statistical approaches to ceramic provenance frequently make use of multivariate methods [18,19,20]. Principal components analysis (PCA) was performed on the log base-10 transformed data set. All elements were incorporated with the exception for Sr and Ni due to an excessive number of samples below the limits of detection. The first seven principal components explain > 90% of the variance in the compositional data set. All PCA results are provided in SI Table 2. The scoring coefficients for each element are representative of that variable's contribution to each principal component. The PCA results indicate that PC1 (33.6% of the variance) is explained by Co, Mn and Mn, and rare earth elements which positively drive variance, while Sb and As negatively drive variance. For PC2 (18.9%), the elements Ba, Mn, and Fe negatively drive the variance. For PC3 (15.9%), Ba and As make strong positive contributions to the variance while Mn, Fe, and Co make negative contributions.

Figures 4 and 5 are biplots of PC1 versus PC2 and PC1 versus PC3, respectively showing the distribution of samples in each clay type. Most Taixi samples show a consistent cluster regardless of color or sampling location. The green Taixi clays are distinct from the main Taixi sample cluster, influenced in part by elevated concentrations of rare earth elements. Specimens from LiShu, Huanglongshan, and Zhau Zhuang are differentiated primarily by As, Sb, and Ba concentrations. One sample from Huanglonshan shows elevated concentrations of some alkali metals, Na, K, Rb, as well as Fe. In both plots, the Zisha potsherds are associated with the Taixi clay samples.

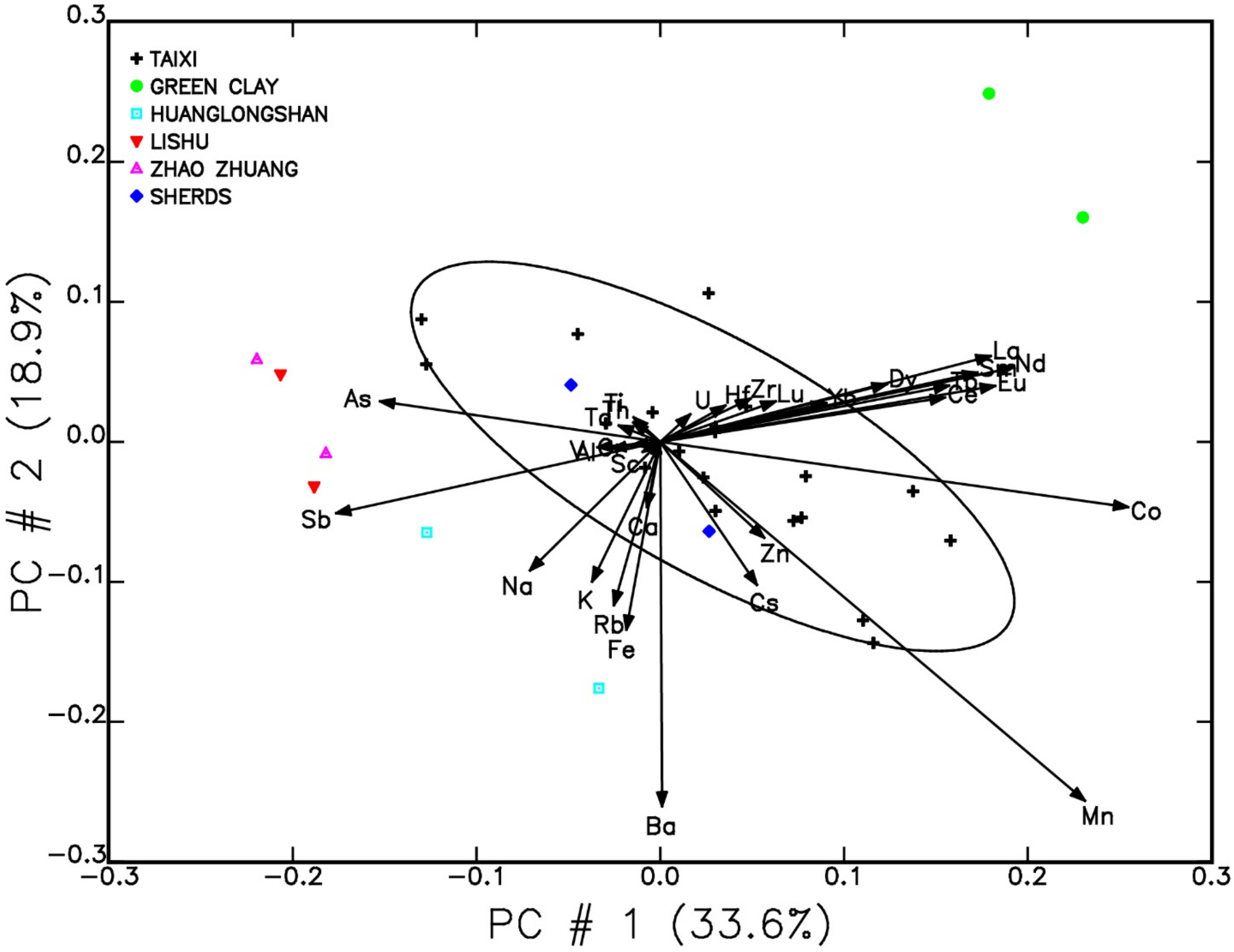

Fig. 4: R-Q mode biplot of PC1 versus PC2 showing samples and element vectors. A 90% confidence ellipse encircles the Taixi samples.

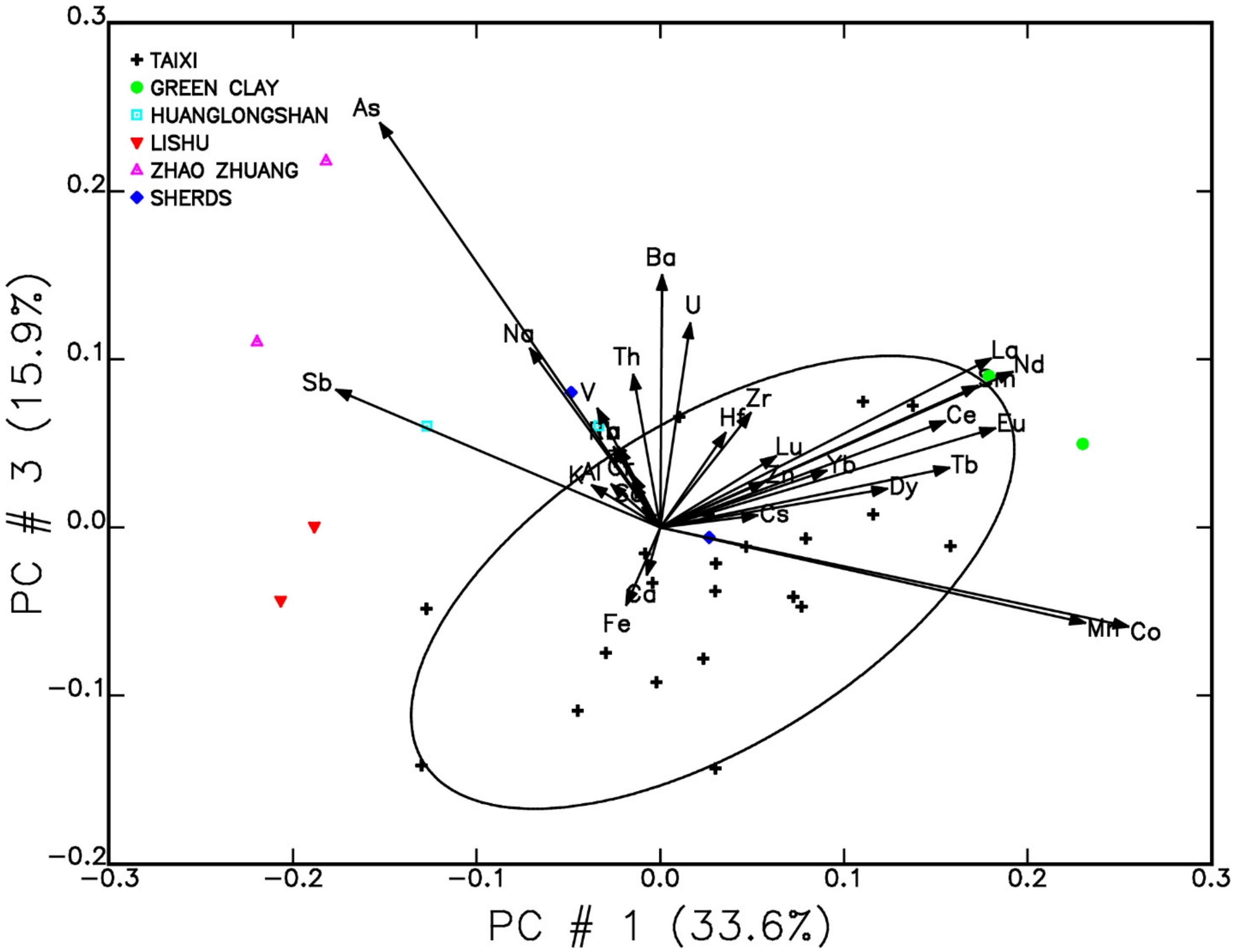

Fig. 5: R-Q mode biplot of PC1 versus PC3 showing samples with element vectors. A 90% confidence ellipse encircles the Taixi samples.

3.2 Petrographic Analysis

Prepared thin sections of Zisha clays were examined by optical petrographic microscope using single polarized and cross-polarized light. Figure 6 shows three selected examples of purple, red, and green clay. The Zisha clays show fewer silt-sized particles (< 5%) than other clay types. The identifiable clay minerals in Zisha clays are sub-angular and rounded quartz (< 0.5 mm), and prismatic particles of muscovite mica (< 0.2 mm). The purple clay has a higher proportion of mica inclusions than the red and green clay. When comparing processed and fired sub-samples, the fired samples showed less mica, and exhibited a denser and more homogeneous clay fabric.

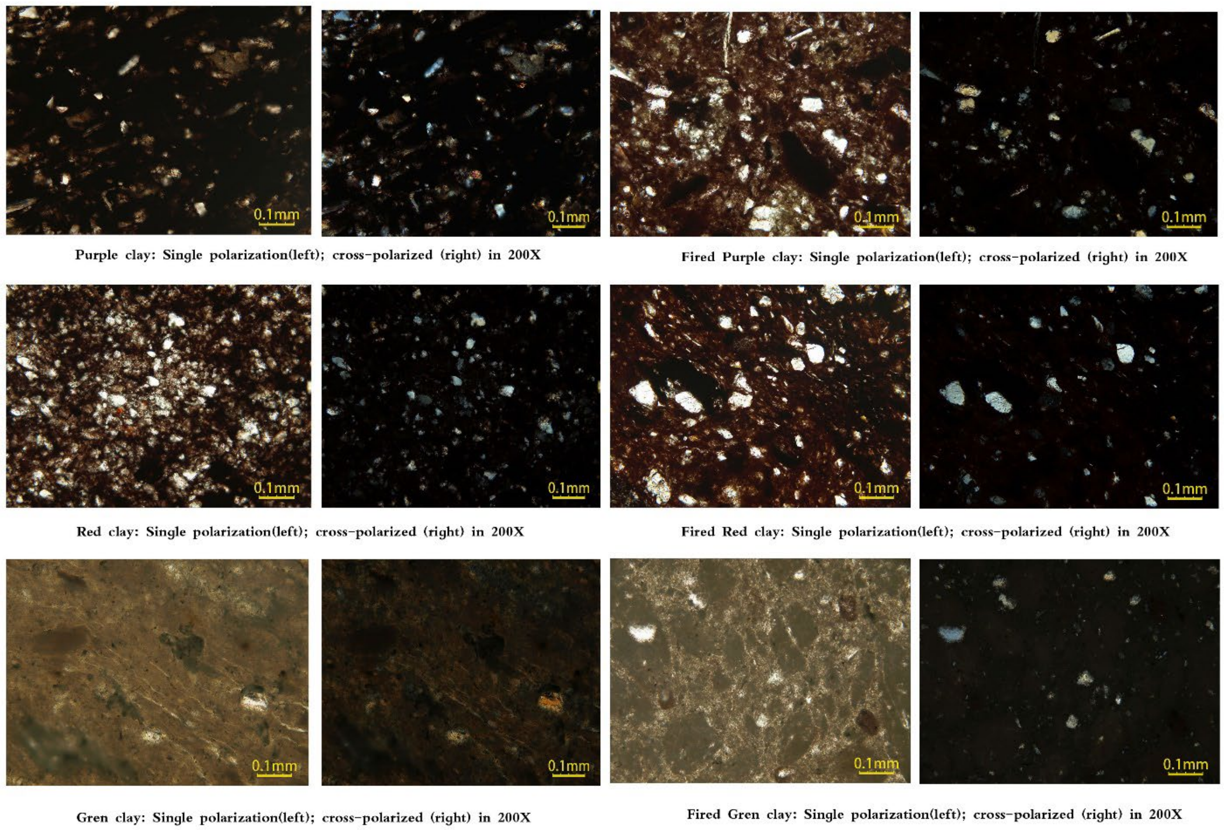

Fig. 6 Petrography results of Zisha Clay samples (Purple, Red and Green)

4.0 Discussion and Conclusions

This study demonstrates several key observations. Previous studies on Yixing clay deposits that used elemental techniques XRF and SEM-EDS were not able to distinguish between the deposits based on major elemental compositions [7, 8, 9]. Here, we have shown that it is possible to differentiate Zisha and other regional clay sources from each other based on a combination of mineralogical and trace element characteristics. In particular, the concentrations of As, Sb, and the rare earth elements have the greatest discriminatory power for distinguishing the clay groups. The Taixi green clays are notably enriched in both light (La, Ce, Nd, Sm, Ce) and heavy (Eu, Tb, Dy, Yb, Lu) rare earth elements. The LiShu and Zhau Zhuang red clays are differentiated from others by concentrations of Sb and As. Those elements are known to readily mobilize during rock weathering [21, 22, 23], which suggests that although the Yixing-area clays are similar in major element composition, variability in clay formation, weathering, and diagenesis are primarily responsible for subtle, localized differences in trace element chemistry. Conversely, some high field strength elements (Zr, Hf, U) and scandium are highly resistant to weathering and alteration, and are often more stable in high silicate materials such as clays [24, 25, 26]. Our data are consistent with those patterns as Sc, Zr, Hf, concentrations are highly stable across all clay groups and did not significantly contribute to geochemical variation between them. We also noted that the red clays from Huanglongshan have elevated levels of alkali earth metals, including Na, K, Rb, and Ba, possibly indicating a different parent rock geologic origin, although more geologic information is required to assess this. Overall, the results show that clays from each sampling vicinity have unique compositional signatures that can be identified by trace element analysis and multivariate statistical approaches.

We have also shown that clays specific to the Taixi mining area appear to exhibit a consistent compositional signature between red and purple clays, with no significant alteration in elemental chemistry from processing and firing. This observation is compatible with the high purity and high-quality characteristics of Zisha clays, and is an important finding for future studies that aim to determine the provenance or authenticity of Zisha stoneware artifacts.

Geochemical fingerprints of clay minerals are an important component of ancient ceramic research. The results of this analysis show that it is possible to infer the origin of Zisha clays through trace element analysis. This is an important finding that sets a foundation for examining larger questions of ancient cultural exchange, object authentication, and the organization of ceramic production in China. Therefore, although the sample size presented here is small, the preliminary results show promise for future provenance studies of Zisha stonewares in archaeological or museum collection contexts.

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