

Insights into the creation of variable-coloured crackle effect in high-fired wares via microchemical analysis of archaeological ceramics from China

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Accepted for publication in *Microscopy and Microanalysis* on 5 July 2022

Abstract

Searching for residue in the glaze of porcelain or stoneware is a difficult task because these glazes are high-fired, well vitrified, and nonporous. This paper analyses the chemical composition of residue observed in glaze cracks of porcelain via SEM-EDS to determine how the crackle effect was produced, in particular, if it was intentionally created during production or the result of post-depositional processes. This study offers insights to a specific type of ancient Chinese porcelain called ‘Ge-type ware’, which has two different types of cracks, and whose origin has been debated for nearly 60 years because it has never been found at any kiln site. This paper analyses the chemical composition of the two crack types, firstly using elemental mapping to ascertain the different mechanism that produced these two crack types of Heirloom Ge ware, and secondly using residue analysis and chemical fingerprinting to determine the provenance of this puzzling type of porcelain. In doing so, this paper demonstrates how the residue in glaze of porcelain can be observed and analysed via microchemical approaches and hopes to inspire more research using this technique in future.

Keywords: Residue; Glaze cracks; Ge-type ware; SEM-EDS

1 Introduction

Residue in ceramics can provide a wealth of information including identifying the former function of the object (e.g. Dunne et al., 2019) or determining its date (Casanova et al., 2020), especially for unglazed ceramic artefacts with large pores that allow for sufficient amounts of residue to be trapped inside the vessel. For glazed ceramics, collecting and analysing residue is a huge challenge as the glaze largely prevents substances from penetrating into the vessel body. Nevertheless, Pecci et al (2016) noted that production flaws or deliberate crackling in certain glazes can allow for organic matter to accumulate even in glazed wares. The present study thus analyses the residue in crackled wares, more specifically the Ge ware, a type of Chinese greenware or celadon dating to the time of the Song (960-1279), Yuan (1271-1368), Ming (1368-1644) and Qing Dynasties (1644-1912) whose date, origin, and production technique are highly contested. Ge ware occurs with two different types of cracks that differ in colour (Figure 1A), and the reasons for these differences in colouring – be they technological or post-depositional – will be at the heart of this paper. This distinctive type of ceramic has never been found at any kiln site, and its provenance has thus been at the centre of a heated debate.

The term Ge-type ware or Ge ware refers primarily to ‘Heirloom Ge ware’ and similar ceramic artefacts with similar ‘double crackle’ features (Shen, 2014), and most scholars distinguish three main types: Heirloom Ge ware, Ming Dynasty Ge ware and Qing Dynasty Ge ware. Heirloom Ge ware was first observed and described by scholars in the 1930s who found them among the Qing Dynasty collections of the Palace Museum in Beijing (Zhou & Zhang, 1964). Heirloom Ge ware was named after a poem

composed by the Qianlong emperor (r. 1711-1799) inscribed on the underside of one of these objects (The Palace Museum, 2017). These poems describes the characteristics of Ge ware which in historical sources has also been named as one of the five great wares of the Song Dynasty (960-1279) (Kerr & Wood, 2004) (Figure 1B). Heirloom Ge ware is characterised by having two different coloured cracks (double crackle), one a thicker black crack and the other a finer brown crack, which have been referred to as 'golden thread and iron wire' (Gompertz, 1958; Geng, 1995). Porcelain with this characteristic has never been found at any kiln site, which is why "heirloom" was added to its name. The number of known Ge-type pieces is extremely small, with no more than 40 held by various museums, most of them in the collections of the Palace Museum in Beijing (The Palace Museum, 2017).

Ming Dynasty Ge ware and Qing Dynasty Ge ware were mainly discovered in tombs as burial objects. They are dated based on the date of the grave, as far as it is known based on epitaphs and other grave content. Both Ming Dynasty Ge ware and Qing Dynasty Ge are hard to distinguished from the Heirloom Ge ware based on visual characteristics, but they can be differentiated by comparing their chemical compositions (Duan, Ding, et al., 2018). Unlike the Ming Dynasty Ge ware and Qing Dynasty Ge ware which can be dated fairly accurately, the origin and date for the Heirloom Ge ware are still unclear. Therefore, its provenance has been under debate for over 40 years.

This paper investigates the residue in the two different coloured cracks of the Ge-type ware to clarify the composition of brown and black residue in the cracks, as well as to explore if the residue were added artificially or accumulated naturally after production. If the coloured cracks were formed by later staining, then it would be misguided to use the double crackle as a feature to find the origin of the Ge-type wares, but if the coloured cracks were made deliberately during production, then they provide insights into the production process and potential origin. For this purpose, the presesnt paper utilizes both LA-ICP-MS and SEM-EDS to observe and analyse the residue trapped in two types of glaze cracks of Ge-type ware.

1.1 Previous understanding of the crackle on Ge-type wares

The formation of glaze cracks is caused by the coefficient of expansion of the clay body being greater than that of the glaze, and often appears when the porcelain cools and shrinks after firing (Lahlil et al., 2013). The causes behind the formation of the black cracks on the Ge-type ware have been discussed by many scholars and there are two main theories, one of natural formation and one of artificial staining (Chen et al., 1984b; Li, 1993; Geng, 1995). The natural formation refers to the iron elements in the black clay body of the Ge-type ware participating in the formation of the cracks (Li, 2021). The artificial staining refers to the black cracks of the Ge-type ware having been artificially dyed and coloured with black pigment (Qiu & Chang, 2016). Based on the principle of thermal expansion and contraction, it has been suggested that Ge-type ware that has just been fired and still retains some warmth, and is then immersed in the black pigment, causing the cracks to burst rapidly and the black pigment to enter the cracks quickly (Li, 2020).

Lahlil et al (2013, 2015) used experimental archaeological to analyse the factors influencing the formation of cracks of Ge-type ware. They found that the thinner the glaze, the higher the density of cracks; furthermore, they observed that cracks will continue forming for up to 20 days after firing (Data in Appendix A: Table A2). Li (2020) combined the results obtained by Lahlil et al (2015) with ethnoarchaeological investigation of the making of Ge-type ware replicas, concluding that the cracks formed naturally and were subsequently stained with black pigment and then left for five days to await for the emergence of new transparent cracks. Once these appeared, the objects were buried in soil to allow the second set of unprotected cracks to be stained brown while the black cracks would remain black. When the objects were retrieved a month later, they thus had two differently coloured sets of cracks. If the black cracks of the Ge-type ware were indeed dyed artificially, then this would have to be

done after firing, which means that this step may have taken place away from the kiln site area. It may have happened close-by or at a greater distance, potentially leading to issues with the identification of the place of production of the Heirloom Ge ware based on scientific analysis of the double crackle features. Nevertheless, so far Li's model of production is only a hypothesis that needs to be tested further, as do suggestions of the crackles having come about naturally after firing or suggestions that it may have happened during firing.

1.2 Archaeological evidence

Exploring the provenance of Ge ware objects will help elucidate trading and exchange networks between various locales, regions, and individuals, and will also provide insights into possible changes over time. The traditional approach has been to conduct typo-chronological studies to explore the origin and date of the ceramics that have no clear provenance (Bishop et al., 1982; Gehres & Querré, 2018). More recently, scholars have been using a combination of typo-chronological methods with chemical fingerprinting to determine the geographical provenance of ceramics (Tochilin et al., 2012; Eiselt et al., 2019; Li et al., 2021). However, the provenance of Ge ware is difficult to establish as such items have never been found in any archaeological excavation. The provenance of this type of porcelain has therefore been controversial since the 1930s when it was discovered at the Qing Dynasty Imperial Palace Collection; hence the name 'Heirloom Ge ware'.

Descriptions of the characteristics of Heirloom Ge ware differ significantly between various historical texts (Chen et al., 1984a; Li, 2020), leading to several different definitions of Ge ware (Kerr & Wood, 2004; Hay, 2010). Different historical texts also propose various theories as to the origin of the Heirloom Ge ware, the most mainstream ones being the following:

- 1) Laohudong kiln site, located at the foot of the Phoenix Mountains in Hangzhou city, was discovered in September 1996. The ancient kiln site stretches over more than 2,000 square metres of flat land. Three dragon kilns, one workshop, two glaze tanks and twenty-four porcelain waste-piles have been found here. Ceramic artefacts bearing the inscription *Xiuneisi* 修内司 have been excavated from the Laohudong kiln site, suggesting that this was a Song Dynasty imperial kiln. The *Zunsheng bajian* 遵生八笺, a text dating to the Ming Dynasty, reports that Ge ware was manufactured in the Phoenix Mountains area in Lin'an city (present-day Hangzhou city), which has convinced many scholars that the Ge ware was from the Laohudong kiln site (Li, 1993; Jiang, 2018).
- 2) Jiaotianxia kiln site, located by Wugui Mountain in the southern suburbs of Hangzhou, has also been cited as potential place of manufacture of Heirloom Ge ware. During three excavations between 1956 and 1985, the remains of one workshop and one dragon kiln were discovered, covering a total area of nearly 1,400 square metres. Some of the ceramics excavated at the site matched the Guan ware (the imperial ware of the Song Dynasty) held in the Palace Museum collections, establishing that this was a Song Dynasty imperial kiln. The *Qingmicang* 清秘藏, a text dating to the Ming Dynasty, claims that the Ge ware is very similar to the Guan ware, which was produced at the Song imperial kilns. This led to the claim that Ge ware, too, was produced at Jiaotianxia kiln (Chen et al., 1984b; Huang et al., 2018).
- 3) Longquan kiln site is another contender for potential place of Ge ware production. The *Chunfengtang suibi* 春风堂随笔, a Ming Dynasty text, says that Ge ware was produced at Liutian kiln, which was supposedly located in the Longquan area. All kiln sites there are now universally known as Longquan kilns, making it one of the largest porcelain kiln sites in China. The main product of the Longquan kilns is celadon, and they have been producing porcelain for over 1600 years, making it one of the longest-established porcelain kilns in Chinese history.

Many researchers believe that the celadon with black clay body and white cracks made in Longquan is the true Ge ware because its features best fit the description of Ge ware provided in various historical texts (Feng, 1981; Wu et al., 2009; Shen, 2014).

Most scholars have assumed that Heirloom Ge ware was produced during the Song Dynasty and have thus focused on documentary evidence to identify the most famous celadon kiln sites of that period (Feng, 1981; Chen et al., 1984b; Li, 1993; Li, 2021). In 2010, with numerous white cracks and a black clay-body and purple edges was found at the Longquan kiln site (Figure 1C). These features are consistent with the characteristics of Ge ware mentioned in historical texts, but they are quite different from Ge-type ware with ‘double crackle’; therefore, scholars have been calling the former ‘Longquan Ge ware.’ It is now generally agreed that Longquan Ge ware is the one recorded in various historical texts since its features match those described in the literature, and it has been named ‘Literature Ge ware’ (Yan et al., 2015). Meanwhile, discussions on the origin of the Heirloom Ge ware has been narrowed down to whether it was produced at the Laohudong or Jiaotianxia kiln site (Figure 1D).

Subsequent discussions on the Ge ware, at several academic conferences, have led to a new understanding of the different types of Ge ware (Xiang, 2012; Jiang, 2018). By now, most scholars distinguish two main types: Ge-type ware, which is characterized by two different-coloured cracks (black and brown); and Longquan Ge ware, which is characterized by a dark green glaze and white cracks and which was produced at the Longquan kilns during the Song Dynasty (Shen, 2014; The Palace Museum, 2017; Duan, Ding, et al., 2018; Qiu & Chang, 2016).

This paper is concerned with the study of the two different-coloured cracks of the Ge-type wares, to analyse the residue in both black and brown cracks and test if they are the same or not. The aim is to deduce if the black cracks of the Ge-type ware were formed artificially. If the crackle dyeing was carried out after firing, then the reason that no kiln site yielded this type of porcelain might be that its features were not formed at the kiln site itself but elsewhere. Furthermore, comparative chemical composition analysis is performed to investigate the origin and date of the Heirloom Ge ware.

2 Materials and Methods

2.1 Samples

The samples used in this work were provided by the laboratory of Ancient Ceramic, Jingdezhen Ceramic Institute, including one piece of Ge-type ware sherd with double crackle (two different colours) and one piece of Guan ware from the Jiaotianxia kiln in the Modern Hangzhou city, Zhejiang Province.

Ge-type ware sample GT-1

GT-1 is a Ge-type ware sherd with two different coloured cracks which was excavated from a Ming-period tomb at Jingdezhen. This particular sample was selected because its date is known, it comes from a secure archaeological context, and the two different coloured cracks (black and brown) in the glaze can be particularly clearly observed (Figure 2A). This sample has a grey-coloured clay body and a white-greenish glaze.

Guan ware sample GW-1

GW-1 is a Guan ware sherd with one coloured crack which was unearthed from the Jiaotianxia kiln site, an imperial kiln of the Song Dynasty. This sample was selected because it has very accurate chronology and provenance information, and because its brown cracks are so pronounced (Figure 2B) that it can be

used for comparative analysis with the brown cracks of the Ge-type ware. The Guan ware sample has a dark-grey clay body and white-greenish glaze.

2.2 Method of analysis

This study first applied established ceramic residue analytical methods, including Gas Chromatography-Mass Spectrometry (GC-MS), to test the chemical compositions of the residue trapped in the glaze cracks. However, the high-fired glaze has a higher degree of vitrification than pottery, resulting in the technical requirements for extracting residue from the cracks being much higher than for extracting residue from low-fired wares which are more commonly the target of residue analysis. The amount of residue the team extracted from the glaze cracks was far below the minimum number of tests required for GC-MS detection.

In order to better characterise the residue composition and its properties, the authors additionally used SEM-EDS and LA-ICP-MS to analyse the residue. The authors also considered to use Raman Spectroscopy for the analysis of the residue areas, but previous results from the Palace Museum using Raman Spectroscopy on the residue of the Ge ware showed that X-ray spectroscopy was unable to establish reliably the C, H, and N content, and that the results could only be normalised to the elements obtained (Duan, Ding, et al., 2018). The authors therefore abandoned the use of Raman spectroscopy for the residue analysis in this case.

2.2.1 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

The pre-treatments of the SEM-EDS analysis, including cutting and polishing test specimens, resin embedding, as well as polishing resin targets, were carried out at the laboratory of Ancient Ceramics, Jingdezhen Ceramic Institute. The samples were cut using a 0.8 mm-thick diamond wire cutter; then the cross-section of the specimens was polished to preserve both the clear glaze layer and the clay body layer. The resin targets were coated with a 10 nm layer of gold.

The analyses of both Ge-type ware and Guan ware samples were performed at the Scanning Electron Microscopy Laboratory of the Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO) at the Chinese Academy of Sciences. The analyses were conducted using a Quanta 400 FEG scanning electron microscopy (SEM) at 20 kV. Energy-dispersive spectroscopy (EDS, Oxford Instruments X-MaxN, UK) and electron backscatter diffraction (EBSD, Oxford Instruments Nordlys nano, UK) were performed on the Quanta 400 FEG SEM at 20 kV to assess the elemental distribution and analyse the composition of selected areas. A X-Max 50 mm² detector and AZtec analysis software supplied by Oxford Instruments were used for EDS elemental analysis. A silicon drift type detector was used, and the detection limit was 0.1% weight percentage from 0.3 to 3 microns depth. The detector had a resolution of 127 FWHM. The ZAF quantification system was used in the software module. Standard-pressure EDS was used for elemental analysis. Primary standards were used to quantify the analysed data of the SEM-EDS, the relevant information of primary standards as well as the accuracy and precision can be found in Appendix A.

2.2.2 LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry)

The bulk chemical analysis for the samples and the residue was conducted by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The analyses were performed at the CAS Key laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, using a Coherent ArF excimer UV 193nm wavelength Laser ablation system (GeoLas pro) coupled with Agilent 7700e quadrupole ICP-MS. The 38-micron spot size and a 10 Hz ablation frequency were used for single spot ablation. The chemical compositional data were calculated using multiple external references without internal standards provided by ICP-MSDataCal, following an approach proposed by Liu Yongsheng and his team in 2008 (Liu et al., 2008).

The reference materials consist of NIST SRM 610 and NIST SRM 612 from the National Institute of Standards and Technology, as well as the USGS (United States Geological Survey) reference glasses BCR-2G, BHVO-2G and BIR-1G. The NIST SRM 610 was used as a monitoring standard. The BCR-2G, BHVO-2G and BIR-1G were used as external calibration standards, and the NIST SRM 612 was used as a secondary standard (Hou et al., 2020). The accuracy and precision, including absolute error, relative error, standard deviation and relative standard deviation achieved by the analyses of the secondary standard NIST SRM 612 for this study are provided in Appendix A: Table A9.

2.2.3 Statistical methods

All comparative plots of chemical composition data in this paper were compared using factor analysis by Principal Component Analysis (PCA), and the principal components included in the PCA were SiO₂, Al₂O₃, CaO, K₂O, MgO and Na₂O. The study conducted Kernel Density Estimation (KDE) combining with PCA to illustrate the distribution of each assemblage using IBM SPSS Statistics 28.0.1. Kernel density estimation is a non-parametric method for estimating the probability density function of a random variable in statistical research (Ma et al., 2022). The KDE mode was conducted on the online statistics platform OxPlot (<https://c14.arch.ox.ac.uk/oxplot/OxPlot.html>)

3 Results

3.1 LA-ICP-MS analysis

3.1.1 Chemical composition fingerprinting of the samples

In order to confirm the type of sample chosen for this study, LA-ICP-MS was used to analyse the chemical composition of the samples. The resultant data as well as the results of previous analyses presented in the scholarly literature were subjected to factor analysis using PCA. The principal components used for the samples were SiO₂, Al₂O₃, CaO, K₂O, MgO and Na₂O.

As mentions above, there are three types of Ge-type ware, including Heirloom Ge ware, Ming Dynasty Ge ware and Qing Dynasty Ge ware. This paper compares the data obtained of the samples analysed in this study using LA-ICP-MS with data from the scholarly literature (Lahlil et al., 2015; Duan, Ding, et al., 2018; Duan, Lyn, et al., 2018; Yan et al., 2015). The chemical composition data of the Ge-type ware (GT-1) collected in this paper shows a composition similar to that of Ming Dynasty Ge ware, which is consistent with the date of the tomb it was excavated from (Figure 3).

The chemical composition of the Guan ware sample (GW-1) this paper collected is similar to that of the ceramics from the Song Dynasty layer of the Jiaotianxia kiln site, confirming it as being a Song Dynasty imperial kiln product. The background information of the two samples was confirmed by chemical composition fingerprinting.

3.1.2. Laser-ablation analysis of the residue in the brown and black cracks

LA-ICP-MS was conducted to obtain elemental data from residue in both brown and black cracks. However, since the sample was resin-embedded in cross-section and the residue in the crack was not perfectly vertical, some information on the surrounding glaze may have been collected accidentally during laser ablating alongside with the content of the crack. To balance out this issue, the LA-ICP-MS data for the residue in the cracks can be combined with the SEM-EDS analysis data for better determining the composition of the residue.

Table 1. The chemical composition of the glaze and residue in cracks of the GT-1 and GW-1 samples.

Name	Type	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	C
		%	%	%	%	%	%	%	%	%	ppm
GT-1	glaze	0.49	0.48	13.99	74.23	3.78	5.78	0.04	0.08	1.09	N/A
GW-1	glaze	0.57	1.22	13.17	64.64	3.11	12.41	0.02	0.11	1.27	N/A
Brown cracks of GW-1	residue	2.06	0.14	26.31	67.71	0.27	0.98	0.01	0.01	2.42	N/A
Brown cracks of GT-1	residue	0.03	0.09	16.42	76.41	2.15	0.76	0.01	0.01	4.01	N/A
Black cracks of GT-1	residue	0.01	6.23	1.14	81.57	1.42	5.24	2.7	1.18	0.46	N/A

As shown in Table 1, both GW-1 and GT-1 have significantly higher Al₂O₃ and SiO₂ content in the brown cracks than in the glaze. The aluminium content of GW-1 is as high as 26.31%. The LA-ICP-MS analysis result for the brown cracks found that the brown residue of GW-1 is a high alumina and high sodium silicate-based material, and the other of GT-1 is a low alumina and high potassium silicate-based material. The residue from the crack in GW-1 has a lower iron content than the crack in GT-1. The residue that entered the cracks of GW-1 is different from those that entered the cracks of GT-1.

In contrast, the data obtained from the residue in the black cracks of GT-1 shows a very unusual phenomenon. In terms of its composition, the black cracks contain residue with very high silica values, as well as magnesium and calcium values of no less than 5%. From the peaks in the elemental profiles, it is worth noting that the silicon and aluminium content is substantially lower than that in the glaze, and it is likely that some components were not effectively detected.

Meanwhile, the residue in the black cracks is likely to be organic matter such as carbon as the concentration levels of elements of the residue are much lower than the values of the elements in the brown cracks. The ICP-MS cannot efficiently ionise the carbon (Riisom et al., 2018). Theoretically, only 1% carbon can be ionised by the ICP, resulting in the sensitivity for the carbon determinations is much lower than metals, metalloids and rare earthen elements (REE) (Luong & Houk, 2003).

In order to double check the composition of the residue in black cracks of GT-1, these LA-ICP-MS data will be discussed in conjunction with the results of the SEM-EDS analysis. To prevent interference with the measurement of organic components, the resin targets containing both GW-1 and GT-1 used in the SEM experiments were coated with gold.

3.2 SEM-EDS analysis of the residue

3.2.1 Brown cracks

A selection of brown cracks in 5 different areas of the Guan ware (GW-1) were analysed using SEM-EDS. Looking at the elemental distribution (Figure 4A), the silicon and aluminium elements show very dense distribution in all analysed cracks. This phenomenon is corroborated by the analytical data obtained via LA-ICP-MS. Silicon oxide in the raw clay material is often higher than in the glaze (Li et al., 2010). The glaze goes through a liquid phase during firing, leading to a more even distribution of all elements. The results of both LA-ICP-MS and SEM-EDS analysis indicate that the residue in the cracks of the GW-1 sample is likely a silicate-based material.

The brown and black cracks of the Ge-type ware (GT-1) were analysed separately by SEM-EDS. When comparing the widths of the brown cracks of GT-1 and GW-1, both were found to be over 400 microns in width in some places but also less than 70 microns in others (Figure 5A and 5B). The crack widths get smaller as they get closer to the surface. The brown cracks on the surface are only about 63 microns wide, resulting in what appears to be a thin width, but the area inside the crack is extensive and is by no means as thin as it appears on the surface. The element mapping images for the brown crack of the Ge-type ware (Figure 4B) show that the residue in the brown crack contains mainly two elements, silicon and aluminium, which are more abundant in the residue than in the glaze. This elemental distribution is similar to the brown cracks of the Guan ware, and also corresponds to the analytical results obtained by LA-ICP-MS. The brown cracks contain almost no carbon, which indicates that the residue in brown cracks in Ge-type ware is also a silicate-based material.

3.2.2 Black cracks

For the black cracks of the Ge-type ware, the residue in them is not only distributed in the cracks, but also in the crevices and voids next to the cracks, which is completely different from the brown cracks. This situation may mean that the original extent of the black residue is smaller compared to that of the brown residue. As shown in Figure 5, on the glaze surface the width of the black cracks is large, measuring over 400 μm , but the width narrows down toward the inside, which is the exact opposite of the brown cracks. On the surface, the black cracks thus appear wider than the brown cracks. Viewing our analysis together with the research by Lahlil et al (2013, 2015) on crack formation in Ge-type ware and Li's (2020) research on the replication of Ge-type ware, we can make some suggestions on the potential causes of this phenomenon. We suggest that the freshly fired ceramics, still warm, were submered into the cool liquid black pigment, causing the glaze to undergo rapid cooling causing cracking, resulting in a wider crack in the glaze starting from the outside. Natural cracking occurring during slow cooling is caused by the fact that the coefficient of expansion of the glaze is lower than that of the paste (Lahlil et al, 2015), and the cracking proceeds from the inside out. The naturally expanding crack is thus larger on the inside and narrower on the surface.

The elemental distribution of the residue in the black cracks of GT-1 is different from that in the brown cracks. The residue in the black cracks contains almost no silicon or aluminium but a large amount of carbon (Figure 4C). The elemental distribution for the black residue is completely different from the results of the LA-ICP-MS analysis. As the sample surface was covered with gold to increase conductivity, it is certain that the carbon was a component of the residue itself.

It is unusual that carbon in organic matter should not be detected using scanning electron microscopy at 20 kV high voltage, suggesting that the carbon observed here came from inorganic material. To test if there is indeed carbon in the residue in the black cracks, the black cracks were analysed using local selected area elemental analysis by EDS. As shown in Figure 6, the chemical composition of the black cracks on average includes 76.48% carbon and 20.98% oxide, while silicon only accounts for 0.46%. The results of the elemental analysis by EDS and elemental distribution for the black residue both indicate that it contains a significant amount of elemental carbon. This suggest that the carbon of the black residue was not effectively ionised in the LA-ICP-MS analysis.

The oxygen content of the black residue is likewise high, but the proportion of silica is low. This suggests that the oxygen is not derived from silica, and that the residue in the black cracks contains carbon-based organic components with a large amount of oxygen. If it is carbon-based organic matter then it likely will not be accurately detected at the high voltage of 20kV. Whether elemental carbon is organic or not will be discussed in detail in conjunction with other studies below.

4 Discussion

4.1 Colouring mechanisms for the two types of cracks

The residue in the brown cracks in both Guan ware and Ge-type ware, shows a similar elemental composition in that their main components are silicon and aluminium with almost no carbon. The brown cracks on the glaze surface of the Guan ware often vary in colour due to the circumstances of burial (Wu et al., 2009). The cracks in freshly fired Guan ware are transparent and colourless, especially for many of the Guan ware objects from the Palace Museum collection which have never been buried and have transparent cracks (Chen et al., 1984a; Wu et al., 2009; Miao et al., 2012). Guan ware was buried in different types of earth of different colouring which produced different-coloured cracks (Chen et al., 1984a). Based on the results of the LA-ICP-MS analysis of the residue in the brown cracks of both samples, the reason that Guan ware (GW-1) and Ge-type ware (GT-1) show different levels of brown colour is most likely due to different types of earth entering the transparent cracks. The residue in brown cracks is likely to be soil from the burial environment (Figure 7).

The residue in black cracks of the Ge-type ware (GT-1) contains a large amount of carbon, and almost no elements other than carbon and oxygen are present in the black cracks. The black cracks are thus not the result of the precipitation of iron from the clay body, as had been previously suggested. The research team at the Palace Museum in Beijing conducted SEM analysis on the Heirloom Ge ware. They did not, however, apply EDS to investigate the elemental distribution in the residue in the black cracks, but they used Raman spectroscopy to test if the residue in the black cracks was organic or inorganic. The results of the latter showed very small amounts of inorganic elements in the residue in the black cracks; therefore, the Palace Museum team suggested that the residue in the black cracks contained a significant amount of carbon. The residue in the black cracks of both Ming Dynasty Ge ware and Heirloom Ge ware is thus likely a carbon-based material or consists of isomers of carbon.

4.2 Residue in the black cracks

As reported above, the compositional analysis of the residue in the black cracks shows that its oxygen content exceeds 15%, and the silica content is around 0.4%. This means that the oxygen measured did not come from the silica but likely derived from carbon-based organisms. According to previous replication studies of Ge-type ware, the modern way of producing the black cracks is to stain them with liquid Chinese inkstick (Li, 2020). Combining the results of the analysis of the residue in the black cracks of the Ge-type ware conducted in this study and the results of previous related research, there is a possibility that the residue in the black cracks of the Ge-type ware is indeed derived from Chinese inkstick which is a mixture of soot and organic adhesive (e.g. animal glue) (Swider et al., 2003).

Unlike conventional Western paints which are often liquid, Chinese ink is traditionally made into solid inksticks from which the ink is liquified by rubbing the stick against an inkstone with a small amount of water (Yang et al., 2019). Soot created from burning wood (typically pinewood) or lampblack made from burning oil using a wick have been the primary sources of carbon used in the production of inksticks for millennia (CUI et al., 2005; Fengye & Liangyuan, 2011; Tang et al., 2019). To produce a strong collagen-based adhesive, animal glue binder, mostly from the skins of animals, is most commonly used (Swider et al., 2003). Considering the overall composition – especially the high level of oxygen –, the colour, and the suggestion made above that the black material may have been in a liquid state when entering the cracks, it appears likely that the material in the black cracks of the Ge-type ware was derived from inkstick instead of carbon minerals.

Nevertheless, if inkstick made with animal glue was used for crackle-staining, then there would have been nitrogen in the residue; however, there is no nitrogen detected by both EDS and LA-ICP-MS analysis. This is probably due to the fact that the animal glue of the inkstick was diluted with water

during the process of making ink, lowering the nitrogen content below the detection limits of EDS and LA-ICP-MS. Likewise, the high-voltage SEM-EDS analysis at 20kV may have burned out the nitrogen. In order to determine whether these black residues are organic or not, more analysis tool such as Py-GC-MS need to be applied. Previous studies on Chinese ink residues (Ren et al., 2018, 2022) have used a combination of Py-GC-MS, Raman spectroscopy and FTIR to analyse the characteristics of different Chinese ink residues. These previous studies have shown that the combination of these three methods is effective in determining whether the carbon-based residues are Chinese ink and – if so – which type of ink has been used. It is hoped that subsequent studies can find a new method to extract the residue trapped in the glaze and obtain sufficient amount of residue to allow for applying these three methods to explore the composition of the black material in the cracks further.

Whether the carbon detected in the analyses describe above is organic or inorganic in origin, the large amount of carbon and oxygen in the residue suggests a completely different mechanism for the formation of black cracks vs that of brown cracks. This type of black residue could not have entered the cracks naturally for instance in post-depositional staining. The black cracks on the Ge-type ware are likely to be artificially stained. Based both on the historical accounts cited above and the results of analyses conducted here and in previous studies, a specific technology of 'crackle-dyeing' must have been part of the chain of production of Ge-type ware.

4.3 'Crackle-dyeing' in the ceramic production chain

Combining the results of this paper with the SEM analysis data of the Ming Dynasty Ge ware and the Palace Museum's analysis of the Heirloom Ge ware (Duan, Lyn, et al., 2018; Duan, Ding, et al., 2018), significant amounts of carbon are present in residue in black cracks in both two kinds of Ge-type ware. The injection of carbon-based material into the cracks does not appear to be the result of chance. As mentioned above, many studies have speculated that the black cracks of the Heirloom Ge ware are anthropogenic. Combined with the results of SEM and elemental composition analysis, it seems plausible that the black cracks were consciously produced using a specific technology that this paper refers to as 'crackle dyeing.'

Previous studies of Ge-type ware cracking have suggested that the formation of cracks is caused by the different expansion coefficients between the glaze and the clay body (Lahlil et al., 2015, 2013). The cracks are formed during the cooling process and can continue forming over a period of 20 days. The thinner the glaze, the more cracks it produces. Previous experimental archaeological research of the Ge-type ware by the lead author of this paper confirmed this result and found that very wide black cracks form when a freshly fired kiln is immersed in a lower temperature ink liquid due to the principle of thermal expansion and contraction (Li, 2020). After the completion of the crackle-dyeing step, new transparent cracks continued to form for over a week, and these new cracks can turn brown after being buried in brown soil, which gives the glaze two differently-coloured crackles (Figure 7). After the black ink has solidified in the cracks, the soil does not enter the already stained cracks at the time of burial because the ink solid fills the stained cracks completely.

The crackle-dyeing step took place after the firing step, which means that there may not have been any ceramics with black cracks at the kiln site as the cracks formed during cooling about one day after firing, and the crackle-dyeing would have taken place after that. It is likely that the potters would have transferred the ceramic to a different location for cooling and subsequent dyeing rather than leaving the wares right by the kiln. Therefore, this paper argues that the search for the provenance for Heirloom Ge ware cannot be based on whether ceramics with similarly two-coloured cracks was excavated from any kiln site. Instead, this paper compares the elemental data of Heirloom Ge ware with ceramic products from various kiln sites to identify the most likely place of production for Heirloom Ge ware.

4.4 Searching the origin of Heirloom Ge ware via comparative chemical analysis

Previous studies have compared the chemical composition of Heirloom Ge ware and wares from kiln sites pointed out as potential places of production in historical texts, including Longquan kiln site, Laohudong kiln site and Jiaotianxia kiln site (Lahlil et al., 2015; Duan, Ding, et al., 2018; Duan, Lyn, et al., 2018; Yan et al., 2015). Li Jiazhi et al (2005) found that the composition of the glaze of the Heirloom Ge ware is similar to that of Yuan Dynasty (1271-1368) ceramics from the in Laohudong kiln site (Figure 8A). They thus suggest that the Heirloom Ge ware is a product of the Laohudong kiln from the Yuan Dynasty and not from the Song Dynasty. This is the first time that a Yuan rather than a Song date has been proposed for these wares.

This suggestion by Li Jiazhi et al (2005) was highly controversial and many scholars vehemently disagreed. Li Yunzhi (2021) pointed out that although the data for the Heirloom Ge ware exhibits similarities to that of the ceramic products from the Laohudong kiln site of the Yuan Dynasty, the number of the samples Li Jiazhi et al (2005) analysed were not sufficient as a basis for determining the origin of the Heirloom Ge ware.

Nevertheless, following the publication by Li Jiazhi et al. (2005), other scholars have started to consider the possibility that the kiln was a product of the Yuan Dynasty. Li Zihan (2020) has combined ethnographic analysis and historical literature on the causes of the Heirloom Ge ware's appearance, arguing that this ware was originally created by Yuan potters as an imitation of Song Dynasty Guan ware. The Yuan potters, so he argues, dyed the cracks to imitate the dark cracks in buried Guan ware. To have a broader basis for sample comparison, the Palace Museum conducted non-destructive portable XRF analysis 30 items from its collection of Heirloom Ge ware, resulting in largely identical readings for all samples (Duan, Lyn, et al., 2018). These readings largely overlap with the ceramics from the Yuan period layer of the Laohudong kiln site (Figure 8B). Duan et al (2018) therefore argue that the Heirloom Ge ware was likely produced at the Laohudong kiln site during the Yuan Dynasty.

Although the ceramic products from the Yuan Dynasty layer of the Laohudong kiln site do not feature two different coloured cracks, the analysis of the residue in the black cracks indicates that these are likely to have been artificially dyed after firing. The wares excavated from the Laohudong kiln site may not have undergone the step of crack-dyeing as they are wasters and rejects that were not deemed fit for sale and usage and thus have not undergone any further processing. This present study therefore posits that Heirloom Ge ware was produced at the Laohudong kiln site, and that it dates to the Yuan rather than the Song Dynasty. The Ge ware that was mentioned as one of the five greatest wares of the Song Dynasty recorded in historical texts thus does not refer to the Ge-type ware discussed and analysed here and in previous studies.

5 Conclusion

This paper applied LA-ICP-MS and SEM-EDS to analyse the microstructure and composition of the residue in glaze cracks of Ge-type ware, finding that both residue and colouring mechanisms of its two types of glaze cracks are completely different. The large amount of carbon and high level of oxygen in the residue in the black cracks of Ge-type ware suggests that the black cracks could have been coloured artificially using carbon-based material, most likely liquid ink derived from Chinese inkstone, using a technique dubbed 'crackle dyeing' in this paper. The residue in the brown cracks of the Guan ware and Ge-type resemble raw clay or soil in composition, and it is thus likely that these cracks obtained their residue and colour during burial from the surrounding earth.

‘Crackle-dyeing’ can only be done after firing, which suggests that the reason Heirloom Ge ware with two types of crackles has never been excavated from any kiln sites is that the ‘crackle dyeing’ process was probably carried out away from the kiln site. Therefore, it is not possible to use two different coloured cracks as a feature to find the location of the kiln that produced Ge-type ware. Based on comparative chemical analysis using both new data and the results of earlier studies, this paper suggests that the Heirloom Ge Ware may have been produced at the Laohudong kiln site during the Yuan Dynasty. All kinds of Ge-type ware could have applied a similar production chain, and the ‘crack-dyeing’ technique may have prevailed during both the Yuan and Ming Dynasties. This paper has shown that residue in glaze cracks can be observed and analysed using SEM-EDS and LA-ICP-MS, and it is hoped that further developments in residue analysis will allow for extracting sufficient material for analysis even from high-fired wares, using for instance FTIR, Py-GC-MS, Raman spectroscopy or supercritical fluid extraction methods, which can then be applied to investigate if the black residue of the Ge-type ware is organic in origin. Furthermore, it is hoped that this paper will inspire more research into residue in glaze cracks to learn about object function and/or production location processes, and materials.

Acknowledgements

We gratefully acknowledge financial support from the Dasong Wuchang Kiln Research Centre for our laboratory research. The authors thank the laboratory of Ancient Ceramic, Jingdezhen Ceramic Institute for authorizing the sampling to carry out this research. The authors also thank Dr Chris Doherty and Mr Qian Ma for technical advice.

Figure Captions

- Figure 1. (A): Characteristic Heirloom Ge ware and its distinctive two-colour crackle features; (B): base engraved with a poem describing the manufacturing process of Ge ware; (C): Longquan Ge ware, also known as ‘Literature Ge ware’, as seen here is characterized by dense white cracks, a black clay body and celadon glaze; (D): Locations of Laohudong, Jiaotianxia kiln and Longquan kiln sites in China (A,B,C from the Palace Museum collection (The Palace Museum, 2017)); D made by the authors using ArcGIS Pro).
- Figure 2. (A): Ge-type ware sample with two different-coloured cracks; (B) Guan ware sample with brown cracks from Jiaotianxia kiln site. The scale bar used for both subpanels is 10 cm in length.
- Figure 3. Factor analysis for the samples analysed in this study compared with data from previous studies (Duan, Ding, et al., 2018; Duan, Lyn, et al., 2018; Miao et al., 2012) (the cited data is compiled in Appendix A: Tables A1-A8).
- Figure 4. Scanning electron microscopy micrographs and energy dispersive X-ray spectroscopy map of most representative elements (Si, Al and C); (A) brown crack of the Guan ware; (B) brown crack in the Ge-type ware; (C) black crack in the Ge-type ware. All samples were secured to the test bench with Cu tape.
- Figure 5. Width measurement of brown and black cracks in both samples in SEM images; (A) brown crack in the Guan ware sample (GW-1); (B) brown crack in the Ge-type ware sample (GT-1); (C) black crack in the Ge-type ware sample (GT-1).
- Figure 6. Chemical composition of the residue in black cracks of the Ge-type ware obtained by EDS analysis; (A) and (B) are the chemical composition of the same area at different scales to demonstrate the reliability of the analytical results.
- Figure 7. Schematic diagram of the residue and colouring mechanisms of two different type of cracks of the Ge-type ware.

Figure 8. (A): Composition factor analysis comparison plot for the glaze of Heirloom Ge ware, Laohudong kiln (Yan et al., 2015) and Jiaotaxia kiln (Miao et al., 2012; 2018). (B): Data of Heirloom Ge ware from the Palace Museum (Li et al., 2005) and its comparison with material from other kiln sites (Yan et al., 2015; Miao et al., 2012; Li et al., 2005) (data from the literature collated in Appendix A: Tables A1-A8).

Appendix Captions

Appendix A. Data obtained from the samples in this study (Table A1) and data collated from the literature (Tables A2-A8). The data are displayed in Figures 3 and 7; Table A9: The accuracy and precision of the secondary standards.

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