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Provenance study of Chinese proto-celadon in Western Han Dynasty

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Abstract

Provenance of Chinese proto-celadon during Shang-Zhou Period has been studied by a lot of scholars. There were two distinct opinions: some scholars claimed that all proto-celadon wares excavated in Northern China were manufactured in Southern China while others believed that both Southern and Northern did produce proto-celadon wares in the same period. Recently, an increasing number of researchers tend to support the viewpoint that proto-celadon has a multi-origin both in Southern China and in Northern China during this period. However, during Han Dynasty few proto-celadon wares and sherds were excavated in Northern China, it seems that all of the proto-celadon products found in Northern China came from Southern China. Several years ago, many huge proto-celadon wares were excavated in Rizhao Cemetery of Shandong Province, and some kilns and proto-celadon sherds were found in Cuipingshan site of Jiangsu Province. Both of the sites locate in Northern China and date to Western Han Dynasty. In this paper, the provenance study of the sherds from these two sites as well as those from Xiaolongjing Cemetery of Zhejiang Province were carried out by the use of dilatometer (DIL) and laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS). It was found that the northern sherds were fired at the temperature around 1200 °C, with higher Fe and Ca concentration but lower Mg content than southern ones, implying the unique manufacture craft in Northern China differing from the southern ones. Our results may suggest that Chinese proto-celadon produced in Western Han Dynasty has multiple producing regions not only in Southern China but also in the north.

Keywords: LA–ICP–MS; DIL; Provenance; Proto-celadon

1. Introduction

The proto-celadon, which is much different from the pottery while close to the porcelain [1–3]), is at the transition stage of ceramic development from pottery to porcelain in ancient China, and is addressed as ''the second milestone in the development history of Chinese ceramics'' [1]. It is widely accepted that the proto-celadon began to emerge in China during Shang Dynasty or even earlier [3,4], and evolved to the so called ''celadon'' invented in late Eastern Han Dynasty period [1]. As to the provenance problem of proto-celadon sherds during Shang-Zhou period, although a few scholars [1,5–7] claimed that proto-celadon wares excavated in Northern China were produced in Southern China and transported to the North for exchange aim, an increasing amount of scholars [8–11] believed that proto-celadon in Northern China might have its own origin and be produced in local area. The multi-origin opinion was supported by other methods such as grading analysis on the body of proto-

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celadon [12], and was prone to be accepted by the academic circle [8].

However, it is in Southern China where celadon vessels first emerged during late Eastern Han Dynasty, and few celadon products were ever found in Northern China from Qin-Han Dynasties to the Northern Dynasty [8]. If proto-celadon did appear in Northern China since Shang-Zhou Dynasties, it is quite strange that this kind of product nearly disappear until the Northern Dynasty. There seemed to be a blank period for the development of porcelain products in Northern China from Qin-Han Dynasties to the Northern Dynasty. Recently, an archaeological suspected kiln site of Western Han Dynasty was discovered in Cuipingshan site in Xuzhou city of Jiangsu Province (Northern China), and the ceramic wares inside bear a strong resemblance to porcelain vessels in appearance. The discovery provided a significant clue for provenance research of proto-celadon products manufactured in Western Han Dynasty, and was hopeful for filling the blank period from Qin-Han Dynasties to the Northern Dynasty in the north.

Previous studies of proto-celadon provenance based on elemental analysis were inclined to focus on the body clay, but the compositional data obtained by different researchers always presented great discrepancies or even contradictions, which is especially prominent for cluster analysis and principal component analysis since products excavated from northern and southern areas fell into the same chemical grouping in some literatures [5,6,13] while separated in some other reports [10,14]. In addition to the body clay, glaze seems to be more suitable for provenance study as a reflection of the producing area information [15]. However, the glaze is only a thin film attached to the surface of the body, and it is difficult to be stripped out for analysis without the interference of the body residues. Laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) is believed to be a suitable method for artifacts analysis due to its micro analysis zone, rapid measure speed, high sensitivity, minor destruction, and low requirement for the shape and size of samples. LA–ICP–MS was widely applied to the analysis of archaeological glasses [16–19] as well as pottery glaze [20], yet glaze study on Chinese porcelain by this method appeared to be never reported before.

To improve our understanding of these ceramic fragments and shed light on the provenance issue of Chinese proto-celadon, we examined these sherds along with the samples unearthed from other two archaeological sites of Western Han Dynasty – Xiaolongjing Cemetery of Zhejiang Province (Southern China) and Rizhao Cemetery of Shandong Province (Northern China) – as comparable experiments by original firing temperature measurement and glaze chemical analysis, with the help of dilatometer instrument and laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS), respectively.

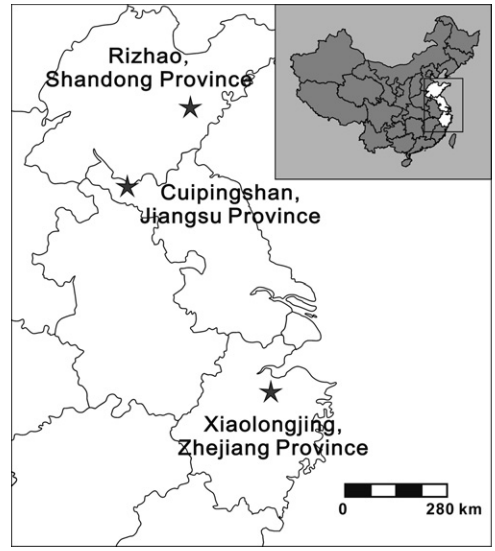

Fig. 1. Locations of Rizhao, Cuipingshan and Xiaolongjing sites.

Fig. 2. A panorama site of Cuipingshan kiln site.

2. Material and methods

2.1. Samples and locations

A total of 25 sherds were obtained from three archaeological sites of Western Han Dynasty: Cuipingshan kiln site, Xiaolongjing Cemetery, and Haiqu Cemetery (Fig. 1). Haiqu Cemetery locates about 1 km away from the south of Haiqu County in the western suburb of Rizhao, Shandong Province. In all, 90 graves were sorted out in this cemetery site during the rescue excavation by Institute of Archaeology of Shandong Province. Xiaolongjing Cemetery was chosen as a comparison site.

Cuipingshan site (Fig. 2), whose outline approached a circle with the diameter of 50–60 m, lay beneath the southwest hillside of Cuipingshan Mountain in Yunlong District of Xuzhou, Jiangsu Province. Two platforms were comprised in this site: The upper one whose diameter is

25–30 m with a cultural layer of about 3 m, and the nether one with a 1.5–2 m cultural layer, indicating a date of Western Han Dynasty. Large amounts of fragments of pottery and proto-celadon vessels, and kiln furniture such as support pins and backbones, were found on the ground, and numerous pellets of slag and burnt soils scattered in the site. The kiln furniture and the firing scale might well manifest its function as a kiln for ceramic firing.

Among the 25 samples, only 13 sherds were selected for glaze analysis by LA–ICP–MS. The rest sherds were abandoned due to the poor preservation of the glaze. On purpose of simplicity, samples excavated from Cuipingshan, Xiaolongjing and Rizhao are denoted as C, X and R.

2.2. Experimental

The coefficient of thermal expansion of a ceramic could reflect its original firing temperature and its quality. For firing temperature measurement, the sample was sliced and ground into cuboid block ($1.5 \times 0.5 \times 0.5$ cm^3). Each block was cleaned using deionized water in the ultrasonic cleaner, and then placed in the sample holder made from Al_2O_3 and set into the Dilatometer of Netzsch-Gerätebau GmbH (Selb, Germany, model: NETZSCH DIL-402C) for heating from room temperature with nitrogen chosen as the purge gas. The heating rate was set to 5 °C/min and the sampling rate was 60 pts/min (16 pts/K). Natural cooling was implemented after the experiment. The Netzsch Proteus-Thermal Analysis Software was exploited to carry out the measurements and evaluate the resulting data.

The instrumentation system at the Missouri University Research Reactor (MURR) comprises a VG axiom double focusing high-resolution ICP–MS connected to a Merchantek 213 nm Nd:YAG laser ablation system. Samplings of the artifacts were conducted by the laser ablation system in the scan mode with a laser beam diameter of 100 μm. Two pre-ablation passes were performed prior to data acquisition to remove possible surface contamination. Each sample was measured on five points in different locations, and average intensity will be used for the next data process.

To obtain quantitative results, some suitable standard samples were selected, including National Institute of Standards and Technology (NIST) standard reference materials SRM 610 and 612, Corning glasses Brill B, C and D. On purpose of ensuring the quality of data, a primary evaluating of these standard reference samples were carried out by linear fit with the signal intensity acquired by LA–ICP–MS and concentration value of all the five standard samples (SRM 612, SRM 610, Brill B, Brill C and Brill D). For a certain element, data of one standard sample will be abandoned if the fitting degree (R^2) of the linear fit is below 0.85, and the linear fit will be processed with the rest four standard materials (Table 1). Concentrations were calculated according to Gratuze [21], Gratuze et al. [22], Neff [23] and Speakman and Neff [24]. More details on the analytical method at MURR and its performance can be found in Popelka-Filcoff et al. [25].

3. Results

3.1. Firing temperature results

Firing temperature data were calculated based on thermal expansion curve obtained by dilatometer instrument which is often employed in heat treatment temperature measurement [26,27]. During the heating process, the size or length of the specimen increases as the temperature rises in the beginning. While the heating temperature is higher than its original firing temperature, the specimen will superimpose a shrinking effect on the basis of linear expansion. Accordingly, there will be a clear inflexion occurring in the expansion curve. In our experiment, the relationship between temperature and change in length $\Delta l_e/l_0$ was detected, where l_0 is the initial length, l_e is the final length, and Δl_e is the length variation ($l_e - l_0$).

The original firing temperature values for these samples from the same site were close of each other. Temperature range of products from Cuipingshan site and Xiaolongjing Cemetery separates from each other with no overlap, and the average value is 1204 °C and 1143 °C, respectively. The lowest temperature of Cuipingshan products (1193 °C) is clearly higher than the highest one of Xiaolongjing sherds (1159 °C). For samples from Rizhao Cemetery, the average temperature (1245 °C) is even higher than that of Cuipingshan ones. All products appear compact in the structure of bodies, consistent with the high firing temperature above 1100 °C. For each site, one typical curve is selected as a representative for presenting the temperature character (Fig. 3).

3.2. LA–ICP–MS results

In contrast to other traditional analytical methods widely applied for archaeological porcelain characterization, LA–ICP–MS provides highly precise more rapidly and expediently [21]. Samples selected for LA–ICP–MS analysis in the present work displayed good preservation of glaze, and the beam diameter was tiny enough compared to the size and thickness of glaze. Consequently, it is assumed that all data are representative of compositional information of glaze without detectable interference from the body, and element concentrations obtained from the same sample ought to be close to each other without large swing. Therefore, data with larger standard deviation could not be accepted. By LA–ICP–MS technique, we measured concentrations of Na, Mg, K, Ca, Ti, Fe, Rb, Sr, Pb, and rare earth elements, which are generally regarded to be significant for reflecting the provenance feature. Actually, only 12 elements were chosen in this paper, which are Na, Mg, K, Ca, Ti, Fe, Sr, Gd, Dy, Ho, Er, and Yb, while the rest were abandoned due to the low content undetectable or large fluctuation of data.

Average concentrations of 10 elements (Na, Mg, Ca, Ti, Fe, Sr, Gd, Dy, Ho, Er, and Yb) are utilized to reflect the overall elemental feature of samples from the three sites.

Table 1
Signal intensity acquired by LA–ICP–MS and concentration value of all the five standard samples (SRM 612, SRM 610, Brill B, Brill C and Brill D). The symbol "–" means that the value, without which the fitting degree (R^2) of the linear fit will be above 0.85, is abandoned due to its negative impact.

	SRM612 intensity (cps) content (ppm)	SRM610 intensity (cps) content (ppm)	Brill D intensity (cps) content (ppm)	Brill C intensity (cps) content (ppm)	Brill B intensity (cps) content (ppm)	Fitting degree (R^2)
Na	484,504	559,244	49,534	7,865	577,317	0.96418
	103,709	99,050	8,902	7,938	126,113	
Mg	339	992	48,496	6,466	–	0.97236
	77	465	23,764	6,212	–	
Al	13,426	17,271	42,726	2,632	36,537	0.98204
	11,164	10,788	28,042	4,603	23,069	
Si	22,773	25,928	16,066	2,230	18,489	0.95334
	335,824	326,833	259,038	168,837	290,850	
K	7,422	6,557	808,960	41,175	76,664	0.93954
	66	486	93,776	23,568	8,299	
Ca	640	760	846	72	520	0.87617
	85,275	81,844	105,790	36,240	61,187	
Ti	29	177	732	–	222	0.99461
	48	434	2,237	–	524	
Cr	334	2,134	259	186	408	0.98073
	40	405	0	0	0	
Mn	237	2,823	30,774	34	9,540	0.97028
	38	433	4,256	0	1,935	
Fe	48	64	450	–	266	0.98091
	56	457	3,634	–	2,376	
Cu	125	1,041	5,890	–	60,556	0.99695
	37	430	3,035	–	21,246	
Zn	52	513	723	136	1,491	0.92641
	38	440	803	418	1,526	
As	34	367	252	1	18	0.9942
	37	317	0	0	0	
Rb	200	2,979	275	96	71	0.99081
	32	431	0	0	0	
Sr	378	2,822	2,382	–	761	0.97648
	76	497	482	–	161	
Y	92	1,539	2	2	1	0.99912
	38	450	0	0	0	
Zr	161	692	263	116	268	0.86039
	36	440	0	0	0	
Nb	106	1,604	3	1	1	0.99912
	38	419	0	0	0	
Cs	184	1,865	1	0	0	0.99957
	42	361	0	0	0	
Ba	17	189	1044	7,172	264	0.98936
	38	424	102,150	102,150	1,075	
La	59	917	2	0	0	0.99969
	36	457	0	0	0	
Ce	105	1,410	3	0	1	0.99983
	38	448	0	0	0	
Pr	102	1,457	0	0	0	0.99966
	37	430	0	0	0	
Eu	35	555	0	0	0	0.99985
	34	461	0	0	0	
Gd	6	89	0	0.99943	0	0.99943
	37	420	0	0	0	
Tb	37	613	0	0	0	0.99942
	36	443	0	0	0	
Dy	8	128	0	0	0	0.99935
	36	426	0	0	0	
Ho	28	476	0	0	0	0.99911
	38	449	0	0	0	
Er	9	149	0	0	0	0.99907
	37	426	0	0	0	
Tm	26	433	0	0	0	0.99877
	38	420	0	0	0	

Table 1 (*continued*)

	SRM612 intensity (cps) content (ppm)	SRM610 intensity (cps) content (ppm)	Brill D intensity (cps) content (ppm)	Brill C intensity (cps) content (ppm)	Brill B intensity (cps) content (ppm)	Fitting degree (R^2)
Yb	9	145	0	0	0	0.9992
	40	462	0	0	0	
Lu	24	392	0	0	0	0.99909
	38	435	0	0	0	
Hf	7	105	1	0	1	0.99919
	35	418	0	0	0	
Pb	48	466	2,069	651,904	4,142	0.99984
	39	413	4,456	340,698	5,663	

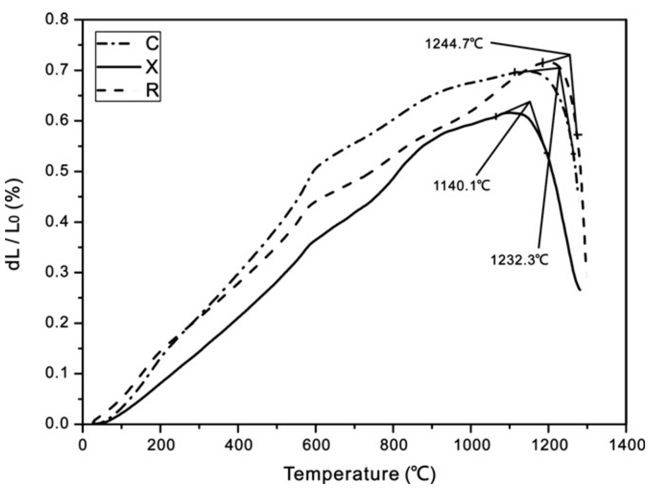

Fig. 3. The dilatometric curve of typical sherds from the three sites.

For intuitive aims, the absolute concentration values are divided by those of samples from Xiaolongjing, Cuipingshan and Rizhao, respectively on purpose of converting all data into the value of the same order. Obviously, Cuipingshan and Rizhao samples show similar chemical feature (Fig. 4a) distinct from Xiaolongjing ones (Fig. 4b and c), illustrating that northern sherds contain more Ca, Fe and less Mg in the glaze than southern ones. As flux elements, concentrations of Mg, K, Na and Fe can well reflect the feature of raw material selection and ancient glaze manufacture process. Utility of bivariate plot might be of great help if we expect to get a further understanding of the individual sample. According to the concentration ratio of magnesium to alkali element (sum of potassium and sodium), products from Cuipingshan and Xiaolongjing are totally separated without overlaps (Fig. 5). The representing spots of Rizhao sherds precisely fall into the Cuipingshan group, indicating that Rizhao samples have similar elemental feature to Cuipingshan sherds. Concentration of Fe impacts the glaze color to a great extent as the glaze appears darker if it contains more Fe [28]. This is in consistent with the appearances of our samples: glaze of Cuipingshan and Rizhao samples looks much more fuscous than Xiaolongjing sherd due to the higher Fe content.

Differences of trace elements, such as Sr, Gd, Dy, Ho and Eu, are also remarkable between samples from Cuipingshan and Xiaolongjing. Average concentration of Sr in Xiaolongjing is much higher than that in Cuipingshan (Table 2). On the contrary, rare earth element (Gd, Dy, Ho, and Eu) concentrations are higher in Cuipingshan samples but lower in Xiaolongjing sherds. As to the Rizhao vessels, the concentration features of these trace elements are similar to Cuipingshan ones in spite of the slightly higher Sr average concentration.

4. Discussion

In previous investigations, scholars seldom provide exact definitions of proto-celadon and porcelain based on chemical and physical reaction occurring in firing process. In this paper, pottery is defined as the mixture of fusible clay and water after drying and firing process at the temperature between 400 °C and 1000 °C. Porcelain or celadon is defined as the material with the body made of Kaolin mineral, or porcelain clay, which is fired at above 1200 °C. The glaze on the surface of the porcelain body is usually of $CaO(MgO)–K_2O(Na_2O)–Al_2O_3–SiO_2$ system, in contrast to the pottery that has no glaze or only has low-fired glaze containing lead element [1]. Proto-celadon is an intermediary product between pottery and porcelain, predating porcelain but fired at the temperature higher than that of pottery. In most cases, researchers distinguished between samples of pottery and proto-celadon according to glaze composition and firing temperature in addition to visual assessment.

4.1. High fired technique

It is inferred that burning events must have taken place in Cuipingshan site, for large amounts of slag and burnt soils were found on the earth surface there. The finding of the pottery and porcelain vessels could hardly confirm that they were just fired in this site because the possibility that they were used as cookers or containers for heating could not be ruled out. However, the large scale of the ceramic number and site area, as well as the discovery of kiln furniture such as support pins and backbones might well convince us of its role as a kiln for ceramic firing. Outdoor firing was impossible for these sherds because of the compact structure of the ceramic body and the high

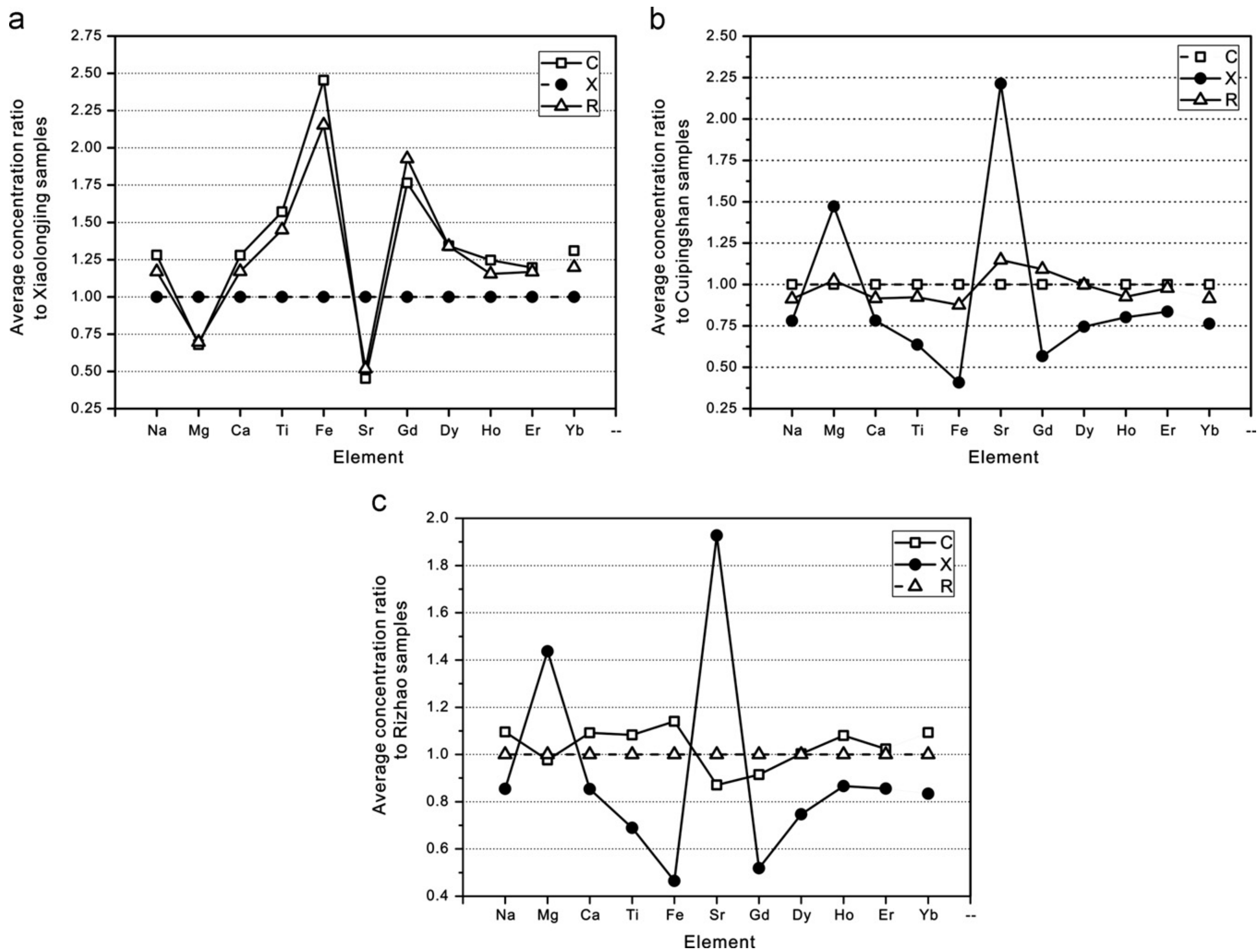

Fig. 4. Average element concentration, standardized by the average concentration of (a) X (Xiaolongjing) samples, (b) C (Cuipingshan) samples, and (c) R (Rizhao) samples.

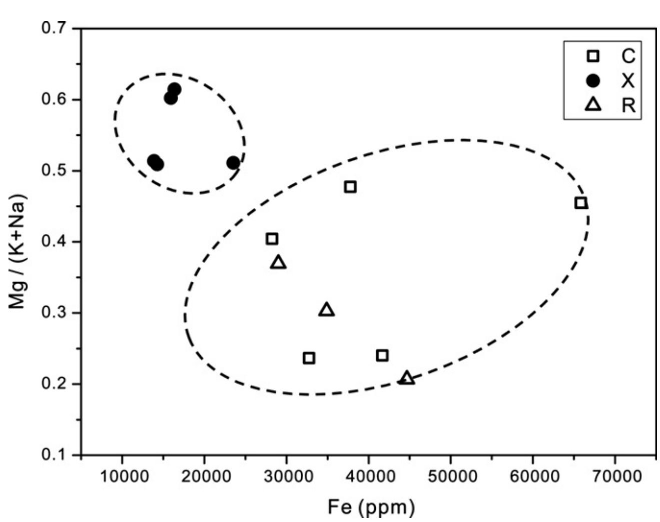

Fig. 5. The bivariate plot of flux elements. The horizontal ordinate stands for the concentration of Fe, and the vertical ordinate represents the ratio of Mg content to K and Na concentration. Ellipses represent 90% confidence levels for group membership.

Table 2
Average concentrations of several representative elements of the samples.

	C (Cuipingshan) (average(ppm)/RSD)	X (Xiaolongjing) (average(ppm)/RSD)	R (Rizhao) (average(ppm)/RSD)
Mg	8407/0.16	12368/0.05	8610/0.57
Fe	41262/0.35	16811/0.23	36192/0.22
Sr	274/0.22	607/0.07	315/0.69
Gd	6/0.17	3/0.19	6/0.09
Dy	6/0.10	4/0.21	6/0.31
Ho	3/0.03	2/0.04	3/0.12
Er	4/0.10	3/0.14	4/0.36

temperature sigh in the kiln [29] which will be discussed below.

Firing temperature statistics of inclusions can reliably reflect the property of a kiln. Previous literature has provided the firing temperature data of some southern sherds from Wucheng (with average value of 1108 °C), Jiaoshan (with average value of 1125 °C), Fanchengdui (with average value of 1080 °C), Dishangang (with average value of 1200 °C), Houshan (with average value of 979 °C) and Zhenjiang (with average value of 1130 °C) [1]. Most of them were fired at the temperature in the range of 1100–1170 °C except three above 1200 °C. By firing temperature data of the sherds, it seems that wares unearthed from Cuipingshan and Rizhao were fired by the technique different from those of most southern kilns.

The advent of glaze, in which the affixion of flux played a vital role, was honored as one of the three breakthroughs in the development of Chinese ceramic [1]. It was generally believed that one of the two primary kinds of flux systems existed in the glaze:$CaO(MgO)–K_2O(Na_2O)–Al_2O_3–SiO_2$ system for high fired glaze and $PbO–Al_2O_3–SiO_2$ system for low fired glaze [1,30,31]. For Chinese low temperature colored glaze of Han and Tang Dynasty, the PbO concentration can be above 40% [32]. In western countries, PbO contents in transparent lead glaze were also as high as 50–70% [33]. Generally, lead glaze is prone to be corroded in the environment and forms several layers of thin films on the surface which seems to be covered by the silver due to the optical interference [32]. In the glaze of our northern samples, however, no lead could be detected, and the glaze surface does not display a silver-like appearance. It can be confirmed that the glaze of sherds from Cuipingshan Kiln and Rizhao Cemetery is high temperature glaze, and craftsmen in Northern China had grasped high temperature technique at that time. It is assured that Cuipingshan Kiln was a porcelain kiln, or at least it did produce porcelain.

Kilns for proto-celadon firing were never found in Northern China before but emerged in several areas in the South, and inclusions unearthed in northern kilns were usually tiles and pottery sherds whose firing temperature were below 1000 °C [1,7,8]. Consequently, porcelain wares unearthed in the North were widely considered to be fired in Southern China. From our results, however, sherds from the northern kiln (Cuipingshan Kiln) have firing temperature higher than the southern products (from Xiaolongjing Cemetery), and the glazes were confirms to be high fired glaze without any lead detected. It is sensible to believe that Cuipingshan Kiln was able to produce porcelain vessels. Notably, as northern products, sherds from Rizhao even have higher temperature than the highest of Cuipingshan samples. Given that Rizhao was discovered as a cemetery of the noble, the inclusions ought to be of better quality than those in the kiln.

4.2. Raw material and manufacture

Flux elements in the glaze are ideal indicators for the raw material selection and manufacture process of porcelain wares. As high fired glaze, the primary flux is lime-based calcium oxide. Previous scholars proposed two patterns of glaze elemental features: high Ca low Fe content system representing plant ash exploiting and the system with high Fe and Ca contents indicating iron-rich clay utilization [13,28]. According to our results, products from the North contain higher concentration of both Ca and Fe but low Mg than that from southern products, and the discrepancy of Fe content is especially significant (Fig. 3a). Northern products characterized by high Ca and Fe concentration were reported before [15], and vessels studied in his work were also suspected to be fired in Northern China.

Concentrations of several trace elements (Sr, Gd, Dy, Ho and Eu) are also quite distinct between northern and southern sherds. Raw materials from adjacent regions share coherent geochemical behavior in these elements, especially rare earth elements, whose formation are dependent on diagenesis and well reveal the local geochemical feature [34,35]. Given that Cuipingshan is confirmed to be the porcelain kiln with high fired technology, it is sensible to consider that samples unearthed from Cuipingshan Kiln might be just fired there. As to Rizhao sherds, we could hardly know the relationship between their firing areas and Cuipingshan Kiln although products from these two sites show similar element feature, because there is no overlap between the firing temperature ranges.

4.3. Development of porcelain in the north

Based on our result, proto-celadon manufacture did exist in Northern China from Shang-Zhou Dynasties to Western Han Dynasty, after which period no evidences of porcelain production were found in Northern China until the Northern Dynasty. However, just in the Northern Dynasty the white porcelain which is of better quality was successfully fired in the north while the white porcelain production did not appeared in Southern China until several hundred years later [1]. It is impossible that proto-celadon in Northern China developed into white porcelain during such a short period in the Northern Dynasty after thousands of years' disappearance since Han Dynasty, and there must be an independent continuous development of porcelain in the north [8].

5. Conclusions

In the present study, body dilatometric analysis and glaze compositional measurements were applied to ceramic products of Western Han Dynasty unearthed from Cuipingshan Kiln, Xiaolongjing Cemetery and Rizhao Cemetery for comparison. Ceramic products excavated from Cuipingshan Kiln, characterized by firing temperature around 1200 °C and low lead content in glaze, are robust evidences for demonstrating that the kiln had its own unique high temperature technology, thus breaking the notion that there were no proto-celadon kilns in Northern China in Western Han Dynasty and filling the blank period from Qin-Han Dynasty to the Northern Dynasty in Northern China. Striking differences also appear in concentrations of several important flux elements as well as rare earth elements: Cuipingshan and Rizhao products contain higher content of Fe and Ca but lower Mg than Xiaolongjing sherds, implying a distinct feature in raw material selecting and vessel firing from southern manufacture. Results of firing temperature and glaze elemental component of proto-celadon products from these three archaeological sites confirm that there was proto-celadon manufacture in Northern China during Western Han Dynasty.

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