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Advances in Lead-Barium-Zinc-Silicate-Type Glazed Warming Bowl Related to the Chinese Xuande Reign (1426–1435)

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Abstract: Diagnostic investigations were carried out on a rare Chinese polychrome glazed ceramic dating back to the reign of the Xuande Emperor (1426–1435). The double-walled warming bowl was investigated using several non-invasive methods such as portable optical microscopy, endoscopy, portable X-ray fluorescence spectrometry, X-radiography, and computed tomography. One microsample was collected and analyzed by scanning electron microscopy with an energy dispersive X-ray detector. According to the results, the chemical composition of the paste suggested a porcelain typology, while the glaze belongs to the lead–barium–silicate (PbO-BaO-ZnO-SiO_2) system. These unexpected data contrast with common knowledge, which attests that the addition of barium in glass and ceramics manufacturing disappeared soon after the Han dynasty (206 BCE-220 CE). Moreover, the combination of PbO-BaO-ZnO-SiO_2 seems to be quite rare both in ancient pre-Han times and during the Ming and Qing dynasties. This paper aims to demonstrate that (a) the use of barium for glaze and glass composition, which seems to have its roots in Taoist alchemy, was not totally halted in later periods compared to the Han dynasty; (b) lead–barium–zinc–silicate glaze was used during the Xuande Emperor's reign. Through a review of ancient Chinese literary sources, we found a lot of unpublished information on the use of barium, lead, and zinc in the production of glazed ceramics during this period. The polychrome glazed warming bowl suggests a particular production that flourished during the brief reign of the Xuande Emperor.

Keywords: double-walled warming bowl; porcelain; lead-zinc-barium-silicate-type glaze; Xuande empire; Chinese technical skill

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1. Introduction

The Investigated Bowl and the Xuande Emperor

The glazed Chinese polychrome porcelain (Figure 1) is a double-walled bowl with a circular hole at the foot to fill the inner part with hot water, keeping both the ceramic and its contents warm. This cavity probably also allowed gas to leak during the firing process, preventing the ceramic from breaking. Three dragons with five claws decorate the front of the bowl, and three dragons are depicted on the back.

According to an imperial edict from the Yuan Dynasty (1279–1368 CE), the iconography of the dragon referred to social class: three claws denoted officers; four claws were for princes; five claws were for members of the imperial court [1]. Consequently, dragons with five claws became characteristic traits of the Emperor of the Yuan Dynasty, a tradition that continued into the Ming Dynasty (1368–1644 CE) [2,3]. The blue mark on the back of the bowl, 大明宣德年製, indicates that it was made between 1426 and 1435, during the Xuande Emperor's reign, belonging to the Ming dynasty. The Xuande bowl typology could therefore be associated with ceramic models called *Zhūgé* (诸葛) and *Kǒngmíng* (孔明), referring to the warming bowls (碗 *wǎn*) with a double bottom made during the Song (960–1279) and Ming (1368–1644) dynasties. In addition to stylistic distinctions, the hole applied to the bottom of the bowl generally showed a difference in size between Song (larger hole) and Ming (smaller hole) ceramics. These names are derived from a folk story that linked these artefacts to the figure of Zhūgě Liàng (诸葛亮, courtesy name 孔明 *Kǒngmíng*), who was an erudite Chinese military strategist during the period of the Three Kingdoms (220–265) [4].

Figure 1. Xuande ceramic warming bowl: (**a**) front view; (**b**) side view; (**c**) back view.

The oldest warming bowl discovered dates back to the Song period and comes from the kilns of Longquan, a city–county located in the southwestern part of the Chinese province of Zhejiang (prefecture of Lishui), famous for its making of celadon [4]. Regarding the function of this type of object, there are different hypotheses, probably due to the Zhuge bowl's uniqueness [5]: it could have served as a practice for ceremonial offerings (供器 *gōngqì*) of libations, or it may have been used daily for heating food and medicines [4]. All these described peculiarities suggest that this rare ceramic type was most likely commissioned by members of the imperial court or high-ranking people.

The Xuande reign is considered by sinologists to be a flourishing period in the arts and a recovery of ancient Taoist traditions [6], due to both the emperor's sensitivity and talent in painting and the arts in general. In the Entertainment Section (《示部》*shì bù*) of the Kangxi Dictionary (《康熙字典》*Kāngxī zìdiǎn*), named after the Kangxi Emperor who ordered its compilation in 1710 during the early Qing Dynasty, Emperor Xuande is described with the following words: 明宣德中賢良示容 "Emperor Xuande of the Ming Dynasty showed his appearance as a virtuous person" [7]. An emperor who was also a painter would have known the pigments and ancient techniques, thus recovering ancient alchemical traditions in the creation of certain mixtures. Therefore, it is of no surprise that during this historical period, considered the golden age of blue and white ceramics, there was also an opening in the sector of polychrome ceramics, which experienced original and widespread popularity. It seems to be not coincidental that Emperor Yingzong, who succeeded Xuande and ascended the throne with the name Zhengtong from 1435 to 1449, issued an edict to ban the private production of colored ceramics [8]. The precise reasons for this prohibition are not explained in Emperor Yingzong's documents (《英宗睿皇帝實錄》*Yīngzōng ruì huángdì shílù*), but it seems almost like an attack on the previous imperial model that had given rise to a short golden period in the recovery of ancient Taoist knowledge.

2. Materials and Methods

Non-invasive and microinvasive investigations were carried on the double-walled warming bowl to enhance knowledge of this very rare artefact.

2.1. Handheld USB Digital Microscope (DM)

Preliminary observations of the ceramic surface were performed using a digital handheld optical microscope, Dino-lite AM7013MZT4 (Dino-Lite Europe, Almere, THE Netherlands) (USB 2.0 interface, CMOS 5-megapixel sensor, equipped with a polarizer, anti-reflection, and IR cut-filter > 650 nm), directly connected to a PC. Images were captured at 50× and 220× magnifications.

2.2. Optical Endoscopy (OE)

A DEPSTECH NTC53 digital optical endoscope (Depstech, London, UK) with a 0.33-inch ultra-thin probe was utilized and connected to a computer via micro-USB to collect images of the interior part of the warming bowl.

2.3. Energy-Dispersive X-ray Fluorescence (ED-XRF)

The XRF measurements were conducted using X-Met 8000 energy-dispersive handheld spectrometer (Oxford Instruments, Abingdon, UK) with an integrated camera (X-Flash SDD detector, 6 mm diameter spot, Rh target X-ray tube operating at both at 8 keV and 50 µA for low-atomic-weight elements and 40 keV, 8 µA for high-atomic-weight elements. The measurement time was 60 s: 44 s at 8 keV to better detect lighter elements, and 16 s at 40 keV for heavier ones, including Sn, Sb, and Ba K-lines. The data, expressed in counts per second (cps), were processed using the Artax Bruker Spectra 7 software (Karlsruhe, Germany).

2.4. Radiography (X-ray) and Computed Tomography (CT)

Radiography (X-ray) and computed tomography (CT) were employed to visualize the inner structure of the bowl. The object was exposed to an X-ray tube (IAE, Bergamo, Italy) at 55 keV, 320 milliampere-seconds, and a distance of 120/150 cm. A 0.010 lead screen was positioned behind the plate to prevent backscatter. X-ray computed tomography was conducted using a TC Supria Hitachi (Hitachi, Tokyo, Japan), with volumetric scanning using the Bone Sharp filter at 120 keV, 200 mAs, FOV 260, thickness 1.25, and a reconstruction index of 0.625. The reconstruction was performed in two planes of space and in 3D with rotation on both the x-axis and y-axis, following the Bone Sharp protocol.

2.5. Sampling

One microsample (CDF1) was collected from irregular glaze edging on the back of the bowl, close to the hole, in accordance with the principle of micro invasiveness.

2.6. Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Detector (SEM/EDX)

Morphological observations and chemical microanalyses on the microsample were conducted using a Hitachi Tabletop TM3030 scanning electron microscope (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer to obtain information on the chemical composition. The microsample was investigated without any preparation by applying it on an aluminum stub with carbon-conductive tape. The analyses were performed at an acceleration voltage ranging from 15 keV to 20 keV with a variable working distance (from 7.3 to 11.4 mm), 40 µA filament current, and a 100 s. acquisition time.

3. Results and Discussion

3.1. The Double-Walled Worming Bowl

Radiography and microcomputed tomography have proven to be valuable tools for understanding both the structure of the double-walled warming bowl and the different materials used in the glaze decoration. According to X-ray images of the frontal and horizontal views of the bowl (Figure 2a–c), the inner and outer diameters are respectively 186.30 mm and 212.04 mm, the base is 86.86 mm, the total height is 77.51 mm, the height of the empty inner part is 16.15 mm, and the hole is 0.5 mm. The maximum thickness is less than 13 mm.

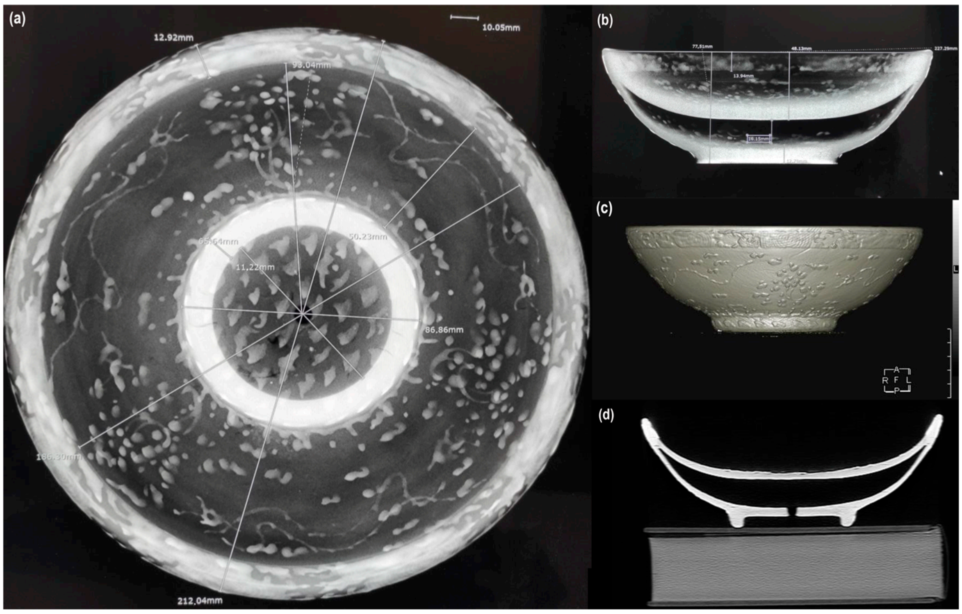

Figure 2. Warming bowl ceramic: (**a**–**c**) X-ray images: frontal and horizontal views; (**d**) CT horizontal images of the bowl. The reconstructions were performed in the two planes of space and in 3D with rotation on both on the x- and y-axes.

The CT reconstruction was performed in two planes of space and in 3D with rotation on both the x- and y-axis (Figure 2d). X-ray and CT images allowed discrimination of heavy metal-based (Pb, Cu) decorations, which appear whiter (Figure 2a,b) and more prominent than the background (Figure 2c) as ED-XRF demonstrated (Table 1). This portable technique is widely used for glazed ceramic and porcelain investigations [9].

The body is not visible but we attempted to analyze the base, where the glaze coating is thinned and abraded, using ED-XRF (Figure 1c). Si, K, Pb, Ca, Fe, Al, Mn, and Ti were detected in this area (Figure 3a,b and Table 1). According to the ED-XRF analysis of the bowl decorations (Figure 3c–l and Table 1), the presence of Pb was identified in all hues, especially in green, yellow, and grey glazes. This element is considered one of the metallic oxide fluxes. Zn is present in small amounts and could be indicative of a raw material impurity rather than a technological choice. Fe and Ca could also be considered impurities or may originate from the body [10]. K maybe related to added fluxing material. Ca content is also associated with the fluxing material added to the glaze, helping to reduce the firing temperature [11]. Ba was detected in most of the investigated areas; this element can act both as an opacifier and a flux [12]. A weak negative correlation between Pb and Ba could suggest a mineralogical association between the two elements, but the possibility of Ba addition cannot be ruled out [13]. Cu, detected in green and greyish decorations (Figure 3c,d,i,j and Table 1), is related to Cu oxide, which is a colorant and also a very active flux well dispersed in the glaze.

The high Fe content suggests it was deliberately added as a colorant, mainly in the red (Figure 3e,f and Table 1) and yellow glazes (Figure 3g,h and Table 1), and it could be considered a strong fluxing colorant. Mn and Fe were used in grey hues (Figure 3i,j and Table 1). In the blue mark on the back of the warming bowl, which appears to be made in underglaze (Figure 3k), Mn together with Fe and low contents of Co were detected (Figure 3l; Table 1). The ratio between the intensities of MnKα and CoKα lines obtained by ED-XRF analysis ranges from 1.92 to 2.59, and the ratio between FeKα and MnKα lines varies from 2.06 to 2.74 (Figure 4a,b).

Table 1. Main chemical composition of the warming bowl determined through ED-XRF (cps *).

Description	Code	Al K12	Si K12	Pb L1	K K12	Ca K12	Ti K12	Ba L1	Mn K12	Fe K12	Co K12	Cu K12	Zn K12
Green edge	cdf1	1	1398	20,042	53	430	1	40	71	197	8	2923	10
Green edge	cdf15	1	759	14,265	11	265	1	33	41	113	5	2090	5
Green drop	cdf6	26	3136	5605	1114	2475	1	192	28	326	3	837	126
Green leaf	cdf13	1	1243	2479	639	1487	1	113	12	220	3	285	78
Green dragon crest	cdf14	3	1304	1976	669	1479	1	116	6	227	4	180	89
Red dragon body	cdf4	7	2286	3569	533	1796	1	163	50	771	4	12	182
Red cloud	cdf16	29	2224	1185	987	2114	1	170	17	310	3	6	125
Red dragon claw	cdf18	1	2231	4564	464	1597	1	141	51	632	9	12	163
Yellow cloud	cdf5	1	2865	10,987	593	1767	2	160	50	314	3	8	110
Grey cloud	cdf7	41	3768	6675	1191	2664	1	209	60	311	5	34	129
Grey cloud	cdf12.1	1	9264	18,082	1901	5159	1	425	331	431	9	15	137
Grey tree	cdf17	13	2151	3168	808	1970	1	164	21	230	3	215	122
Grey tree	cdf17.1	1	5113	5477	1351	3954	1	365	114	263	1	145	105
Blue mark	cdf8	252	6971	228	2738	4404	1	322	118	324	58	8	350
Blue mark	cdf11	223	6308	225	2701	4458	1	327	147	303	69	8	353
Blue mark	cdf12	271	7588	193	3056	4949	1	361	132	350	51	7	357
Blue mark	cdf19	99	3833	153	1972	3230	1	245	92	248	48	7	271
Blue mark	cdf20	54	2636	283	1498	2446	1	176	29	216	5	34	219
White background	cdf2	233	6712	184	2784	4518	1	328	69	310	12	8	357
White background	cdf9	119	4869	1109	1914	3655	1	276	51	338	3	44	156
White background	cdf10	1	2301	14,583	228	975	5	103	40	363	3	7	106
White background	cdf16.1	1	4634	3391	1082	3827	16	329	105	523	6	153	141
Base of the bowl	cdf3	437	3288	816	2274	1153	49	72	161	695	8	20	91

* The data are expressed in counts per second (cps).

According to several scholars, the pigments used in Chinese blue glazes changed in composition over time. Therefore, Fe, Mn, and Co ratios have been utilized as a tool to discriminate between different ceramic chronologies because the absolute concentration or amount of these chromophore elements is not meaningful (ref. [9] and references therein, ref. [14] and references therein). Yu and Miao [9] demonstrated that lower Mn and higher Fe contents distinguish imported Co blue raw materials from Chinese ones. A Mn/Fe ratio< or >0.35 was employed to discriminate the porcelains of the Xuande period (lower ratios) from those of the Kangxi, Yongzheng, and Qianlong periods (higher ratios). According to Wen et al. [14], the Fe/Mn value in the early Ming period (Hongwu–Yongle, 368–1424) is higher than 11, in the Middle Ming period (Xuande–Hongzhi, 1426–1505 CE) it is lower than 2.5, and in the Late Ming period (Zhengde–Wanli, 1506–1620) the ratio is between 3 and 10. The comparison of the Fe/Mn ratios of the blue hues of the investigated double-walled warming bowl with the literature data [9,13–15] suggests the use of imported Co-based raw material (Figure 4a,b).

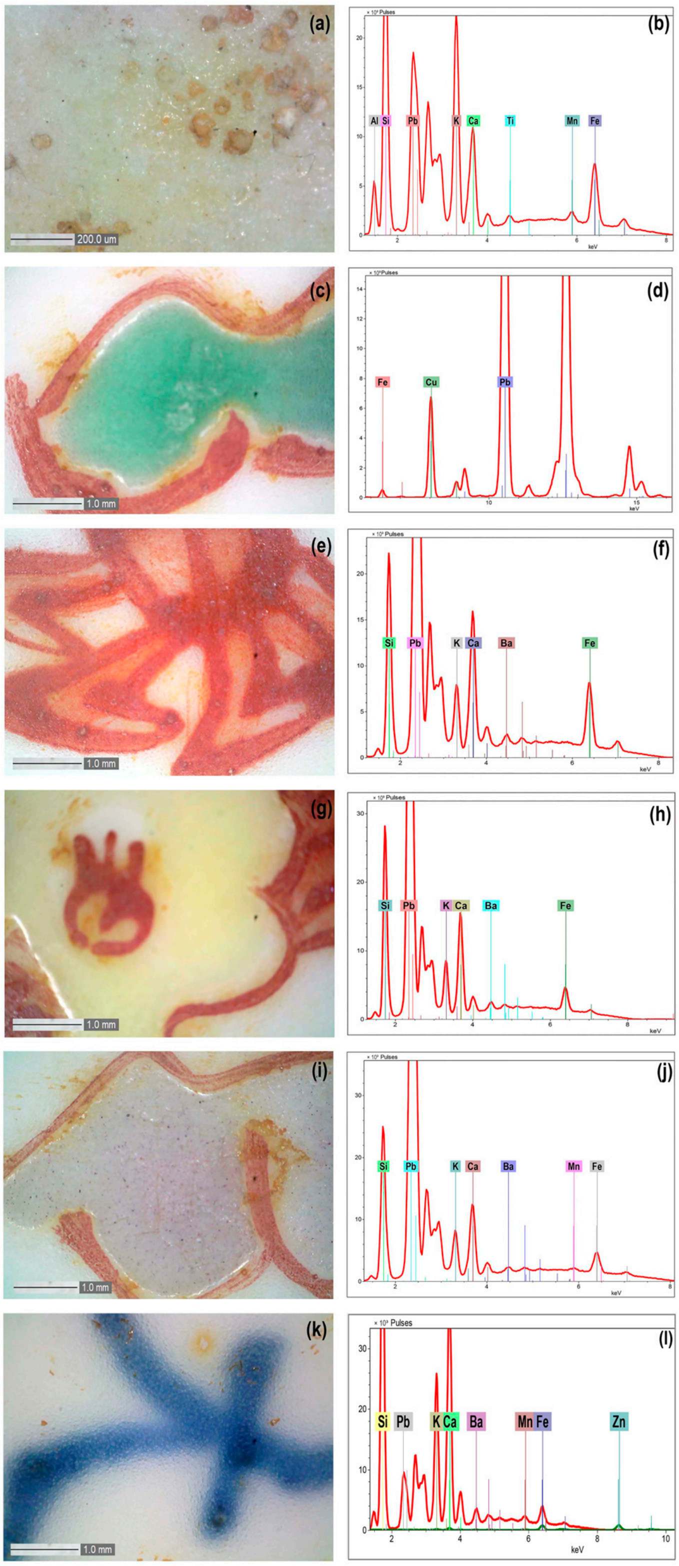

Figure 3. (**a**) Digital micrograph; (**b**) ED-XRF spectrum recorded on the base of the bowl; (**c**) Digital micrograph; (**d**) ED-XRF spectrum recorded from the green decoration; (**e**) Digital micrograph; (**f**) ED-XRF spectrum recorded from the red decoration; (**g**) Digital micrograph; (**h**) ED-XRF spectrum recorded from the yellow decoration; (**i**) Digital micrograph; (**j**) ED-XRF spectrum recorded from the grey decoration; (**k**) Digital micrograph; (**l**) ED-XRF spectrum recorded from the blue mark. ED-XRF spot diameter is 6 mm.

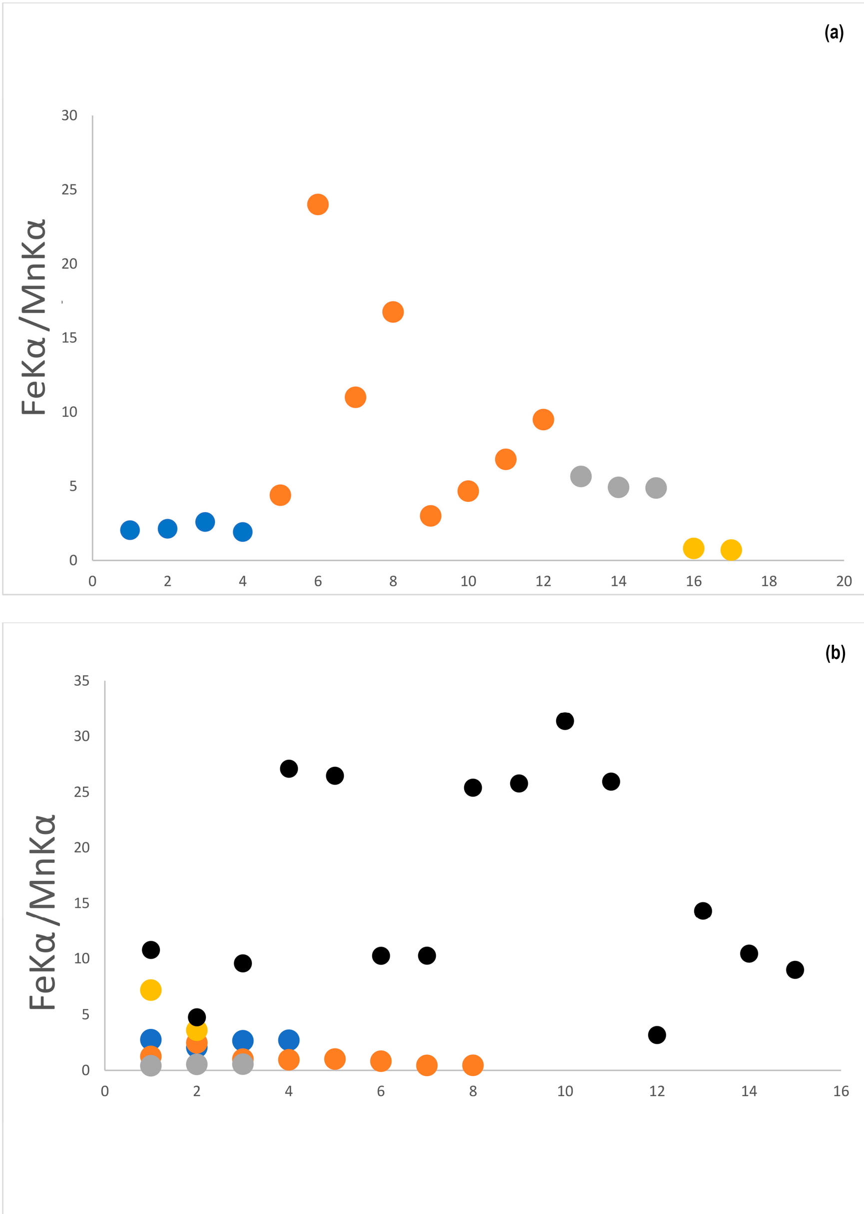

Figure 4. Ratios between the intensities of (**a**) MnKα and CoKα lines; (**b**) FeKα and MnKα lines for the blue mark of warming bowl (solid blue circle) obtained by ED-XRF analysis, compared with the data of You and Miao [9] (solid black circles), Wood [13] (solid yellow circles), Wen et al. [14] (solid orange circles), Feng and BaoRu [15] (solid grey circles).

Moreover, local Co sources were used in the Middle Ming Dynasty while in the Xuande period, the Co used for imperial porcelains was mainly imported, but sometimes a mixture of local and non-local pigments is attested.

Due to the limitations of the ED-XRF technique, it is not easy to determine the specific nature of the body and glaze. However, SEM/EDS analysis of the microsample collected from the edge of the hole made it possible to formulate some hypotheses about its composition. The ceramic paste (Figure 5a,b) is mainly composed of Si and Al, with minor amounts of K, Ca, Fe, Na, and Mg suggesting a porcelain typology [16]. The presence of Si, Pb, Ba, and Zn (Figure 5c,d) was confirmed, indicating that the glaze belongs to the lead–barium–zinc–silicate (PbO-BaO-ZnO-SiO_2) system.

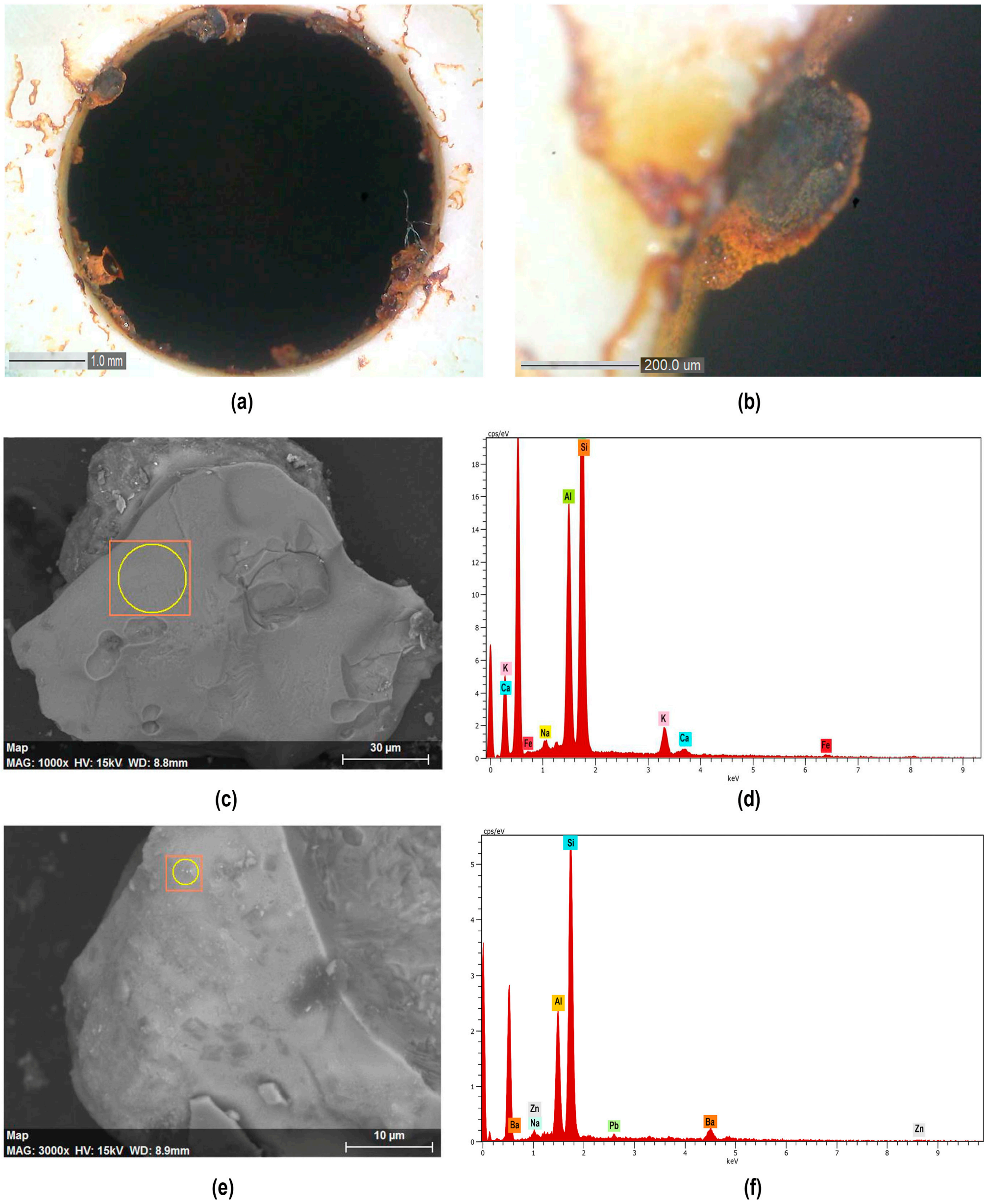

Figure 5. Base of the warming bowl: (**a**) Hole with irregular glaze edges, digital micrograph; (**b**) detail of the sampled area (sample CDF1); (**c**) SEM micrograph and (**d**) EDS microanalysis of the body; (**e**) SEM micrograph and (**f**) EDS microanalysis of the glaze edge. The investigated areas are indicated with a circle inside a square.

These unexpected data contrast with common knowledge that suggests the addition of barium-bearing material to early Chinese glasses and glazes to achieve a jade-color opacity [17–21] documented during the early Warring States period (453 BCE–221 CE) and then disappearing soon after the Han Dynasty (206 BCE–220 CE) [22,23].

While lead–barium mixtures in glazes are an unusual composition following the Han Dynasty, the combination of lead and zinc also appears to be quite rare, both in the early pre-Han phases and during the Ming and Qing dynasties. An example related to lead–zinc comes from a monochrome red porcelain from the Ming Dynasty, the Yongle period (1402–1424), preserved at the Victoria and Albert Museum [13]. The presence of Pb-Ba-Zn glazes was also detected in Jingdezhen blue and white porcelains from the Yuan, Ming, and Qing dynasties [24]. A glazed ceramic imported from Bahlā, a large oasis city in central Oman, dating back to the 17th century, represents the first evidence in the production of

Pb-Ba glaze in the Islamic world, standing out from contemporary traditions and having no parallels in Near East glaze production [25].

The strong correlation between PbO and BaO implies that they are mineralogically associated, suggesting the exploitation of a single source for the lead–barium material. Notably, the presence of a glaze of lead–zinc–barium type in which BaO does not show any correlation with PbO indicates only in this case the use of different raw materials [25]. Anyway, the presence of Pb-Zn could suggest the exploitation of a single source for the lead-zinc raw material. Pb-Zn-Fe mineralizations, in which the main minerals are galena, calamine, and limonite/goethite, are well known [26]. Minerals containing lead, barium, and zinc were found in several Chinese deposits such as those of Jinding, Lehong, and Huize [27–30].

3.2. The Chinese Texts on the Use of Barium, Lead, and Zinc

Scholars agree that lead–barium glass [31] was invented in China during the Warring States period (453 BCE–221 CE), hypothesizing that this processing technique, employed in the creation of glass and ceramic glazes, suddenly disappeared right after the Han Dynasty (206 BCE–220 CE) [23,32]. Additionally, there is a belief that ancient Chinese texts do not provide clear indications regarding the use of lead–barium or even just barium in the production of glass and ceramics [23,32]. Until now, all research conducted on lead–barium glasses and ceramic glazes spans from the beginning of the Warring States period (5th century BCE) to the end of the Han period (2nd–3rd century CE). It is a firm conviction that this glassmaking method did not continue into subsequent eras, seemingly inexplicably forgotten, possibly due to the spread of Confucianism gaining more ground over Taoism [33]. Various arguments support the idea that the lead–barium mixture was rooted in Taoist tradition, as suggested by modern archaeological studies [34,35]. It is believed that the southern kingdom of Chu was once a production center of lead–barium glasses [18,21,36,37]. This theory could be further strengthened by discoveries of ancient lead–barium glasses [38,39] and modern findings of barite deposits mainly concentrated in southern China [30]. Additionally, the occurrence of mineral deposits containing lead and barium in the Henan and Hunan provinces [40] supports the association of this glassmaking tradition with Taoism. It is worth noting that the kingdom of Chu, considered by other Chinese ethnic groups as inhabited by barbarian populations, was the birthplace and the primary center of diffusion of Taoism. This region is also the birthplace of the legendary founding master Laozi, the author of the first and most significant Taoist text, 《道德經》 *Dàodéjīng* (*The Tao Te Ching*).

Based on our advanced research on ancient texts, we found that barium was used in the ceramic manufacturing technique in subsequent periods long after the early Warring States period and the Han Dynasty [23,32]. The dictionary 《康熙字典》 Kāngxī zìdiǎn (Kangxi Dictionary) in chapter seven 《金部》Jīn bù (Golden section) [7] mentions barium, citing two other dictionaries and an exegetic book: 鋇: 《廣韻》布蓋切《集韻》博蓋切, 音貝. 《博雅》鋌也. "Barium (鋇 bèi): Guǎngyùn in phonetic means distend and cover; Jíyùn in phonetic means distend and cover but also ciprea shells; bóyǎ: ore". This clearly explains the phonetic (反切 fǎnqiè) of the two characters with the meanings of stretch (布 bù and 博 bó) and cover (蓋 gài) related to barium in the ceramic context, as an element that acts as a binder for colors and glazes that stretch over the surface of the biscuit, thus covering the surface of the ceramic for the second low-temperature firing.

Moreover, all the information provided by the aforementioned dictionaries is specifically directed to the use of barium in the field of ceramics, in times much later than the Warring States period (453 BCE–221 CE) and the Han Dynasty (206 BCE–220 CE).

In the volume 《卷三百五八》 *juǎn sānbǎi wǔbā* (*Three hundred fifty-eight*) of the 《全唐文》 *Quán Táng wén* (*Complete Tang Dynasty*) [41], it is written: 夫霸者鋇酪玻蓋白黑雜合, 不純用德焉. "Mighty men produce a mixture of fermented barium to obtain glass coated in white and black, which is an impure use of virtue". The text refers to an operation carried out by Taoist alchemists, namely the creation of glass pendants worn on belts or necklaces imitating jade. In ancient times, gentlemen wore jade to show their social status, to which specific virtues were attached.

The importance of barium is highlighted in numerous sources from the 16th to the 19th century indicating that only men of a certain rank and social influence could possess such wealth [41–44]. For instance, in the 《警世通言》 *Jǐngshì tōng yán* (*Warning Words*), a compilation of novels and folk stories in forty volumes by Feng Menglong [44], a situation is described: 承祖父之遺業, 家藏鋇數萬, 以財豪稱子鄉裡. "Inheriting the ancestral business, the family hoarded tens of thousands of barium, and because of their wealth, the son was hailed as a hero in his hometown". In the 《皇朝經世文編》 *Huángcháo jīngshì wén biān* (*Classic of the Emperors of the World*), a monumental collection of essays from the late Qing Dynasty [42], it is written: 人拳鋇街處 "the strong man resides on the street of barium". Moreover, in a Southern Song Dynasty book 《宋朝事實》 *Sòngcháo shìshí* (*Facts of the Song Dynasty*) [43], it is narrated that in the third year of Yongxi, during a military festival (軍節 *jūn jié*) held in Yongqing County, a man called Fangzhou was offered barium as a promotion (升鋇 *shēng bèi*, literally "rise to barium").

In different circumstances, some powerful Chinese families even used a mixture of barium to punish wrongdoers, as described in a passage from the 《全上古三代秦漢三國六朝文》 *Quán shànggǔ Sāndài Qín Hàn Sānguó Liùcháo wén* (*The Complete Texts of Three Ancient Dynasties, Qin, Han, Three Kingdoms and Six Dynasties*) [45], in which is mentioned a decoction (鰲 *àn*), made with the plant ricinus (蓖 *bì*) and dark barium or secret barium (暗鋇 *àn bèi*), prepared and used specifically to punish transgressors.

In the section 《地數》 *De shù* (*Terrestrial Numbers*) of the famous 《管子》 *Guǎnzi* (*Book of Master Guan*) [46], there is an interesting expression, 鈓銀 *zhù yín* "silvered metal", which can refer to numerous metals of this coloration. Excluding silver, precisely written in the text with the character 銀 *yín* (and not 鈓銀 *zhù yín*), these two characters could be related to all other silvered metals, including barium, as described in the text 《警世通言》 *Jǐngshì tōng yán* (*Warning Words*) [44]: 翠香、翠紅各賞衣服一套, 折鋇銀三兩. "Cuixiang and Cuihong rewarded each with a set of robes and three barium silver *liang* (a weight measurement corresponding to 1/20 of a kilogram)".

The dictionary 《廣韻》 *Guǎngyùn* states, under the word barium: 鋇柔鋌也 "also a soft ingot of barium" [47], which indicates the similarity between barium and the silvery-white metal 柔 *róu* (soft).

In a novel from 1814 titled 《天豹圖》 *Tiān bào tú* (*Tianbao's Illustration*), barium is again associated with silver when a man called Huā Sàijīn says: 就是往尋銀鋇 "I was about to go looking for silvered barium".

It is possible that the silvered metal (鈓銀 *zhù yín*) and the sentence 上有鉛者, 其下有鈓銀 "where there is lead above, there is silvered metal below" mentioned in the 《管子》 *Guǎnzi* (*Book of Master Guan*) [46] could indeed refer to both barium and the lead/barium association. Two metals, therefore, lead and barium, were used together to produce glass (imitating jade) and ceramic glazes.

Chinese craftsmanship in glass and ceramic production, like many other forms of art and crafts, has maintained a close connection with Taoist alchemy over the centuries, despite efforts by Confucian intellectuals to hinder its spread, especially in courtly circles. The term "elixir" (丹 *dān*) is commonly used to describe methods for glass and ceramic manufacture. During the Xuande reign (1426–1435), we find this same expression once again in relation to the use of lead in the production of ceramic tiles and the coloring of tripod vessels [48].

Now, returning to the text from the 《管子》 *Guǎnzi* [46], Goushan (苟山), a specific mountain rich in minerals and metals, is mentioned. It is not easy to pinpoint which Goushan the ancient Chinese referred to, considering that even today it is a fairly common name in China, encompassing at least five places located in various districts (Qinzhou District, Tianshui Prefecture, Gansu Province; Wushan County, Tianshui Prefecture, Gansu Province; Li County, Longnan Prefecture, Gansu Province; Pujiang County, Chengdu Prefecture, Sichuan Province; Heshan County, Jiangmen Prefecture, Guangdong Province), plus other mountains with the character 苟 *Gǒu* contained in their names, such as Tanggoushan (Rongshui Miao Autonomous County, Liuzhou Prefecture, Guangxi Zhuang Autonomous Region), Goudaoshan (Xinfeng County, Shaoguan Prefecture, Guangdong Province), and Huanggoushan (not to be confused with the homophonic Huanggoushan in Sui County, Suizhou Prefecture, Hubei Province). Huanggoushan is located approximately 25 km southeast of Baishan City and 20 km west of Linjiang City (near the border with North Korea), where there is a deposit of Zn-Pb carbonate (zinc–lead). This deposit was discovered in 1959 and the exploitation ceased over ten years ago. According to Wang et al. [49], the deposit contains a remaining reserve of 110,000 tons of Zn and 18,000 tons of Pb with average grades of 9.08% Zn and 1.22% Pb. Minerals containing lead, barium, and zinc were found in various deposits as well as in Jinding [27], Lehong [28], and Huize [30].

Regarding the history of zinc in China, in the 《天工開物》 *Tiāngōng Kāiwù* (*The Exploitation of the Works of Nature*), a scientific and technological text written by Song Yingxing published in 1637 [50], zinc is mentioned and referred to as 倭鉛 *wō qiān*, translated as "Japanese lead". The term is not intended to indicate the metal's origin from Japan (where it is known as あえん in Japanese) but serves as a metaphor to describe its strength, vigor, and hardness compared to lead, which has a softer consistency. The passage states: 凡倭鉛古書本無之, 乃近世所立名色. 其質用爐甘石熬煉而成. 繁產山西太行山一帶, 而荊、衡為次之. 每爐甘石十斤, 裝載入一泥罐內, 封裹泥固以漸砑幹, 勿使見火拆裂. 然後逐層用煤炭餅墊盛, 其底鋪薪, 發火煅紅. 罐中爐甘石熔化成團, 冷定毀罐取出. 每十耗去其二, 即倭鉛也. 此物無銅收伏, 入火即成煙飛去. 以其似鉛而性猛, 故名之曰倭雲. The expression 倭鉛 wō qiān (Japanese lead, to indicate zinc), mentioned by Song Yingxing [50], does not appear in ancient texts because the name and color were established in modern times. The use of this substance derives from the processes of firing and refining calamine. It is found abundantly in the Taixing Mountains of Shanxi, followed by Jing and Heng. To bake ten jin (1 斤 *jīn* = 0.5 kg) of calamine, place it inside a terracotta jar, seal with clay, and let it dry slowly to prevent cracking at the sight of fire. Then fill it in layers with coal cakes, the bottom of which is paved with firewood, increasing the fire until it reaches the melting point for calcination. The calamine in the container at the center of the kiln melts into a sphere, is extracted when cooled and stabilized, then the jar is broken. This substance stabilizes without copper, and when subjected to fire, it ascends and becomes volatile like steam. Since it is similar to lead but has a more vigorous nature, it is called "Japanese cloud".

In the Chinese language, the character indicating zinc is still 鋅 *xīn* today, but its presence in the ancient documents is extremely rare. It was mentioned in very few texts such as the 《康熙字典》 *Kāngxī zìdiǎn* (*Kangxi Dictionary*) in the third and seventh parts of the 《金部》*Jīn bù* (*Golden section*) [7], in which zinc was defined as 剛 *gān* (strong) because this metal has a great hardness, more than tin and lead. The same quality is reiterated in the translated passage from 《天工開物》 *Tiāngōng Kāiwù* (*The Exploitation of the Works of Nature*) with the character 猛 *měng* (strong, vigorous), as Song Yingxing says, "it is similar to lead but has a more vigorous nature" [50]. The strong nature of this metal is then called 倭雲 *wō yún* (Japanese cloud). In the West, this metal was named in various ways, and Antonio Campana, in his Farmacopea [51], provides the following list: *Oxydum zinci*, *Oxydum zinci sublimatum*, *Oxydum (deuto)zinci*, *Oxydum (per)zinci*, *Oxydum zinci album*, *Flores zinci*, *Lana philosophica*, *Calamina*, *Nihil album*, *Lapis calaminaris*, *Pompholix*, *Zincum calcinatum sublimatum*, *Tutia praeparata*. These terms, including, in particular, that of "lana philosophica", which can be easily equated with 倭雲 *wō yún* ("Japanese cloud"), all refer to zinc oxide obtained by melting zinc until it boils. The vapors released into the air transform into fluffy white flakes, which are then collected. Alchemists exploited the combustion of this metal with air to prepare the so-called "philosophical wool" or, in Chinese, "Japanese cloud".

Concerning the use of zinc during the Ming period and the early years of the Qing Dynasty (between 1400 and 1700), some scholars [17,52], using ancient maps, identified ancient calamine mines predominantly in southern China. The excavations and archaeological investigations conducted since 2004 in zinc smelting sites in the upper and middle

Yangtze River region confirmed the widespread use of lead–zinc minerals during the Ming Dynasty [30,53]. These scholars recognized three smelting sites: the banks of the Yangtze River, the Qiyao Mountain region, and the Wu River region in Youyang County.

4. Conclusions

The double-walled porcelain bowl could be associated with patterns called (诸葛) *Zhūgé* and (孔明) *Kǒngmíng*, referring to the warming bowls (碗 *wǎn*) made during the Ming Dynasty (1368–1644).

The glazes belong to the lead-zinc-barium-silicate (PbO-BaO-Zn-SiO_2) system, suggesting a particular production that thrived during the short reign of the Emperor Xuande. The green color originates from the dissolution of Cu in the glassy matrix; Fe was used to obtain red and yellow hues; Mn was utilized in the grey detail and together with Fe in the blue mark, whose Fe/Mn ratios suggest the use of imported Co-based raw material.

Starting from the review of ancient Chinese literary sources, we found much unpublished information on both the use of barium and lead/zinc in the production of glazed ceramics over time and the location of ancient mines in southern China.

Although everything points to a rare piece concerning the lead–barium–zinc–silicate-type glazed warming bowl, it would be a mistake to believe that in the Xuande period, there could be no other ceramics with this composition. It is not entirely unfounded to suspect that during this short reign under an enlightened emperor, certain ancient production techniques originating from Taoist alchemy experienced a revival.

The results of this research should represent an incentive to further investigate other similar double-walled warming bowls preserved in various museums and private collections.

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