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The Origin of Ko-Kutani Porcelain: New Discoveries and a Reassessment

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Abstract: The origin of Ko-Kutani porcelain and its decoration style have been debated for over a century. Despite the well-established theory that identified the wares as the result of porcelain production in Kaga (present-day Ishikawa Prefecture) in the 17th century, there still is no general agreement as to where they were first incepted and fired. In recent years, curatorial traditional criteria have formed the basis upon which a new theory has been gaining popularity in Japan, identifying Arita (present-day Saga Prefecture) as their actual place of birth. Such a new theory, however, has proven insufficient to cast new light on many of the unexplained facts that characterize the history of the wares. Furthermore, scientific evidence has been lacking, as no systematic analyses of the porcelains were carried out until the present work. In order to define univocally the dynamics behind this period of Japanese history, the most important and complete Ko-Kutani collection extant in Japan today (Ishikawa Prefectural Museum of Art) was analyzed by portable X-ray fluorescence (pXRF). The scientific investigation was also extended to the very scarce shards excavated at the Kaga kiln site and Nonomura Ninsei's masterpieces. For the first time ever, the results herein presented clarify the missing points crucial to reaching a definitive conclusion.

Keywords: Ko-Kutani; Nonomura Ninsei; Enamel; Smalt; Porcelain; Jesuit Mission; XRF; Japan; Kaga; Pigment

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1. Introduction

The origin of Ko-Kutani porcelain and its decoration style have been debated for over a century. Despite the well-established theory that identified the wares as the result of porcelain production in Kaga (present-day Ishikawa Prefecture) around the late 1640s and mid-1650s, there still is no general agreement as to where they were first incepted and fired. In recent years, curatorial traditional criteria have formed the basis upon which a new theory has been gaining popularity in Japan, identifying Arita (present-day Saga Prefecture) as their actual place of birth [1–3]. Such a new theory, however, has proven insufficient to cast light on many of the unexplained facts that characterize the history of the wares, including the inception of the innovative decoration style that set apart Ko-Kutani wares from Arita porcelains.

Furthermore, scientific evidence has been lacking, as no systematic analyses of the porcelains were carried out until the present work. In order to define univocally the dynamics behind this period of Japanese history, the most important and complete Ko-Kutani collection extant in Japan today (Important Cultural Properties of Ishikawa Prefecture—Ishikawa Prefectural Museum of Art) has been analyzed by means of portable X-ray fluorescence spectroscopy (pXRF). The analysis was also extended to Nonomura Ninsei's Incense Burner in the Shape of a Pheasant (National Treasure of Japan—Ishikawa Prefectural Museum of Art), Nonomura Ninesi's water jar (Important Cultural Property of Japan—Ishikawa Prefectural Museum of Art) and the very scarce shards excavated at the Kaga kiln site (Ishikawa Archaeological Foundation).

The choice of using pXRF spectroscopy to analyze the wares has twofold reasons: the impossibility of taking samples from the artworks and the proven effectiveness of the technique, in many cases, in obtaining chemical information in a totally non-invasive, no-touch and on-site modality, a mandatory requirement for the scientific investigation to be authorized. For the first time ever, the results herein presented clarify the missing points crucial to reaching a definitive conclusion.

2. Materials and Method

2.1. Analyzed Porcelains and Ceramics

The analyzed Ko-Kutani porcelains belong to the Collection of the Ishikawa Prefectural Museum of Art, Kanazawa, Japan, and most of them are designated as Important Cultural Properties of Ishikawa Prefecture. Nonomura Ninsei's Incense Burner in the Shape of a Pheasant (*Koro*—designated as a National Treasure of Japan), Water Jar (*Mizusashi*—designated as Important Cultural Property of Japan) and Incense Container (*Kogo*) also belong to the collection of the Ishikawa Prefectural Museum of Art. The shards have been provided by the Ishikawa Archaeological Foundation, Kanazawa, Japan.

2.2. XRF Spectrometer: Methodological Approach, Experimental and Measurement Parameters

XRF analysis finds a wide application in Heritage Science activities and research thanks to its high capability to efficiently, and in a non-destructive way, identify chemical elements (with atomic numbers higher than sodium $Z > 11$) in a single measurement of the investigated surface, combined with the spectrometer's portability. X-ray fluorescence spectroscopy is a powerful tool that indeed represents today one of the most applied techniques for Cultural Heritage elemental material characterization, due to its user-friendliness and its versatility of application on the multiple types of materials that can constitute a find or a work of art [4].

Generally, the XRF results obtained by using a portable spectrometer are basically to be considered semi-quantitative, even with a supposedly homogeneous matrix or known stratigraphy. However, in the case of chromophore identification constituting an enamel or pictorial layer on different topologies of support, not only is the qualitative level of the data provided by XRF analysis sufficient to achieve the archaeometric objectives, but it is also improved by the determination of the characteristic emission peaks ratio of the marker chemical elements. In fact, this technique has been successfully and efficiently applied to layered samples [5,6], evaluating both the thickness and depth of distribution of chemical elements in multilayered structures by measuring $K\alpha/K\beta$, $L\alpha/L\beta$ and $L\alpha/L\gamma$ X-ray ratios in pigment layers in paintings and gilded or silvered alloys (the depths of element calculation is available online at https://xrfcheck.bruker.com/InfoDepth—URL accessed on 1 September 2024).

It is well known that the intensity ratio becomes higher as the layer thickness increases, because the attenuation coefficient of the $K\alpha$ ($L\alpha$) line is larger than that of the $K\beta$ ($L\beta$) line. Considering the analyzed matrices and the characteristic emission energies of the chemical elements for glaze and enamel identification, the analysis depth is typically within a thickness of 40 μm for a lead-rich glaze and within 500 μm for a lime–alkali glaze, the variability depending on the heterogeneity of the materials (in terms of the glaze thickness and the concentration of the chromophores).

In the analyzed finds, the similar chemical matrices of the analyzed blue and green enamel layers and the similar intensity values detected on the same typology of chromophores for all the collected XRF spectra have been verified. For this reason, the characteristic peaks related to the same chemical element can be considered directly comparable for each of the analyzed layers.

Coherently, the present study has employed just such a methodological approach and has provided objective parameters by which Smalt-based blue and green coloring agents on selected Japanese porcelains can be compared, all through the systematic analysis of the X-ray K-line ratios of the marker elements of Smalt, specifically Mn-Co and Co-Ni for blue enamel and Cu-Zn for green enamel.

The employed XRF portable instrument consists of a miniature X-ray tube system (Amptek, X-123 SDD, Mini-X X-ray tube, Bedford, MA, USA), which includes the X-ray tube (max voltage of 50 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics, and the USB communication for remote control; a silicon drift detector with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line energy resolution (depends on peaking time and temperature); 1 keV to 40 keV detection range of energy; max rate of counts to 5.6×10^5 cps; and software for acquiring and processing the XRF spectra.

The primary beam and detector axis form an angle of 0 and 40 degrees, respectively, with the perpendicular to the sample surface. The measurement parameters were as follows: tube voltage 35 kV, current 80 μA, acquisition time 100 s; no filter applied between the X-ray tube and the sample; and distance between sample and detector of around 1 cm. The setup parameters were selected to have a good spectral signal and to optimize the signal-to-noise ratio. Measurement data were processed using the factory-provided data reduction DPPMCA software Version 1,0,0,22, which enables acquisition, display and control for Amptek signal processors and allows the automatic peak recognition supported by manual peak selection and checking. The software further enables curve fitting based on chosen elements to ensure a match between the measured spectra and the theoretically predicted spectra calculated from fundamental parameters. XRF spectra have been graphically provided by Origin Pro 8.5.

Three consecutive measurements on the same enameled areas were repeated for each of the analyzed examples in order to obtain the average values for the intensity ratios of the XRF signals of the chemical elements for the overglaze blue (Mn/Co; Co/Ni) and overglaze green (Cu/Zn) enamels.

The error of the calculated intensity ratios has been verified as below 5%. In the case of a partial overlap of the XRF signals of the characteristic lines (FeKβ—CoKα; CoKβ—NiKα) the emission peaks have been subjected to a deconvolution process to obtain the intensity value of the element of interest for the calculation of the elemental ratio.

3. Results and Discussion

Taking into consideration the exceptional importance of the collection and the groundbreaking evidence emerging from this first-time-ever scientific study, the results are presented on a piece-by-piece basis: spectra of the most relevant materials are reported in the respective sections for each of the Ko-Kutani porcelains (19 pieces), Nonomura Ninsei's vessels (3 pieces) and the excavated shards (4 pieces).

Moreover, the wares are listed in the order of their firing, from earliest to latest: the timeline is based on the three main periods identified in the paper, that is, the Early Period (1648–1650), the Middle Period (1650–1651) and the Late Period (1651–1655). Such an approach enables a deeper understanding of the historical context and its associated materials and distinctive decoration schemes.

The results are also summarized in Table 1: the images, decoration motif, period of production, chemical compositions of blue and green enamels, identified pigments and ratios of the most relevant elements are listed for each of the analyzed masterpieces and excavated shards.

Table 1. Chemical elements detected by X-ray fluorescence (XRF) on the multiple points analyzed for each color, along with the corresponding hypothesized pigments: **Major** and (minor or trace elements); underlined elements identify the chromophore.

Analyzed Porcelains and Ceramics	Description	Historical Period	XRF Results: Enamel Matrix and Chromophores	Identified Pigments	Co/Ni Ratio (Blue)	Cu/Zn Ratio (Green)
 	Shallow bowl with design of *Hotei*	Early Period (1648–1650)	Green Enamel **Pb**, **Cu**, K, Si (Fe, Ca, Zn, As, Ni, Mn, Ti, Ca)	**Cu-Zn-As Green**	**-**	**27.12**
 	Shallow bowl with design of *Phoenix*	Early Period (1648–1650)	Blue Enamel **Pb**, **K**, Si (Cu, Fe, Co, Ni, As, Ti, Ca) Green Enamel **Pb**, **Cu**, K, Si (Fe, Ca, Zn, As, Ni, Mn, Ti)	**Smalt Blue** **Cu-Zn-As Green**	**1.16**	**14.9**
	Nonomura Ninsei Incense burner in the Shape of a Pheasant (*Koro*) (National Treasure)	Early Period (1648–1650)	Blue Enamel **Pb**, **K**, **Cu**, Si (Fe, Co, Ni, As, Mn, Ti, Ca) Green Enamel **Pb**, **Cu**, K, Fe, Ca, Si, Au* (Zn, Ti, Mn, Ni, Al) * Au from overlapping gold decoration	**Smalt Blue** **Cu-Zn Green**	**2.15**	**6.7**
 	Shallow bowl with design of *Scattered Treasures* and *Heron*	Middle Period (1650–1651)	Green Enamel **Pb**, **Cu**, K, Si (Fe, Ca, Zn, As, Ni, Ti, Ca)	**Cu-Zn-As Green**	**-**	**20.4**
 	Shallow bowl with design of *Quail*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K**, Si (Cu, Fe, Co, Ni, As, Ti, Ca) Green Enamel **Pb**, **Cu**, K, Si (Fe, Zn, As, Ni, Mn, Ti, Ca)	**Smalt Blue** **Cu-Zn-As Green**	**1.52**	**22.9**
 	Shallow bowl with *Paving Stone Pattern*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K** (Cu, Fe, Co, Ni, As, Si, Zn, Ti, Al, Ca) Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, As, Ni, Mn, Ti, Si, Ca)	**Smalt Blue** **Cu-Zn-As Green**	**1.6**	**19.5**

Table 1. *Cont.*

Analyzed Porcelains and Ceramics	Description	Historical Period	XRF Results: Enamel Matrix and Chromophores	Identified Pigments	Co/Ni Ratio (Blue)	Cu/Zn Ratio (Green)
	Shallow bowl with design of *Peonies in Overglaze Enamels* (*Iro-e Botan*)	Middle Period (1650–1651)	Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, As, Ni, Mn, Ti, Si)	**Cu-Zn-As Green**	**-**	**29.89**
	Shallow bowl with design of *Flowers and Bird Inside Jar*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K** (Cu, Fe, Co, Ni, As, Si, Zn, Ti, Ca) Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, As, Ni, Mn, Ti, Si, Ca)	**Smalt Blue** **Cu-Zn-As Green**	**1.2**	**16.5**
	Shallow bowl with design of *Stream and Mandarin Duck*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K** (Cu, Fe, Co, Ni, As, Zn, Si, Ti, Ca) Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, As, Ni, Ti, Mn, Ca)	**Smalt Blue** **Cu-Zn-As Green**	**1.17**	**26.48**
	Shallow bowl with design of *Scattered Flowers and Twin Birds*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K** (Si, Cu, Fe, Co, Ni, As, Ti, Zn, Ca) Green Enamel **Pb**, **Cu**, **K** (Fe, Si, Zn, As, Ni, Mn, Ti, Ca)	**Smalt Blue** **Cu-Zn-As Green**	**1.15**	**22.12**
	Shallow bowl with design of *Karuta and Cranes*	Middle Period (1650–1651)	Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, As, Ni, Mn, Ti, Ca)	**Cu-Zn-As Green**	**-**	**22.9**
	Shallow bowl with design of *Old Tree and White Cloud*	Middle Period (1650–1651)	Blue Enamel **Pb**, **K**, **Fe**, **Cu** (Zn, Mn**, Co, Ni, As, Ti, Si, Ca, Al) ** from black decoartion layer Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, As, Si, Ni, Ti, Si)	**Smalt Blue** **Cu-Zn-As Green**	**1.14**	**18.92**

Table 1. *Cont.*

Analyzed Porcelains and Ceramics	Description	Historical Period	XRF Results: Enamel Matrix and Chromophores	Identified Pigments	Co/Ni Ratio (Blue)	Cu/Zn Ratio (Green)
	Nonomura Ninsei Water Jar for the tea ceremony, *Mizusahsi* (Important Cultural Property)	1650–1655	Green Enamel **Pb**, **Cu** (Si, Fe, K, Ca, Zn, Ni, Ti, Mn, Ca, Al) Cold Gold Pigment **Au**, **Ca** (Fe, Cu, Si, K, Ni, Ti, Al)	**Cu-Zn Green** **Cold Gold Pigment**	**-**	**22.3**
	Nonomura Ninsei Incense Container, *Kogo*	1650–1655	Blue Enamel **Pb**, **Cu**, **K** (Si, Fe, Co, Ni, As, Zn, Ca, Al) Green Enamel **Pb**, **Cu**, **K** (Si, Ca, Fe, Zn, Mn, Ti, Ni, Al)	**Smalt Blue** **Cu-Zn Green**	**0.76**	**14.3**
 	Shallow bowl with design of *Shochikubai*	Late Period (1651)	Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, As, Ti, Ni, Si)	**Cu-Zn-As Green**	**-**	**18.73**
 	Shallow bowl with design of *Peony*	Late Period (1651–1652)	Green Enamel **Pb**, **Cu**, **Zn**, **K** (Fe, As, Mn, Si, Ti, Ni, Ca)	**Cu-Zn-As Green**	**-**	**5.5**
 	Shallow bowl with design of *Aged (Aode) Pine Tree*	Late Period (1651–1652)	Green Enamel **Pb**, **Cu**, **K**, **Zn** (As, Fe, Si, Mn, Ni, Ti, Ca)	**Cu-Zn-As Green**	**-**	**4.96**

Table 1. *Cont.*

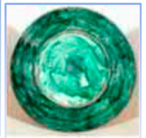
Analyzed Porcelains and Ceramics	Description	Historical Period	XRF Results: Enamel Matrix and Chromophores	Identified Pigments	Co/Ni Ratio (Blue)	Cu/Zn Ratio (Green)
 	Shallow bowl with design of *Pine Tree and Peacock*	Late Period (1652)	Blue Enamel **Pb**, **Cu**, **K** (Si, Fe, Co, Ni, As, Zn, TiCa) Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, Ni, Ti, Mn, Ca)	**Smalt Blue** **Cu-Zn Green**	**1.19**	**21.14**
 	Shallow bowl with design of *Chestnuts and Waves*	Late Period (1652–1653)	Blue Enamel **Pb**, **K**, **Cu** (Si, Fe, Co, Ni, As, Zn, Ti, Ca, Al, Mn) Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, Ni, Ti, Ca)	**Smalt Blue** **Cu-Zn Green**	**1.14**	**30.03**
 	Shallow bowl with design of *Scattered Cherry Blossoms*	Late Period (1653–1654)	Blue Enamel **Pb**, **K**, **Cu** (Fe, Co, Ni, As, Si, Ti, Ca) Green Enamel **Pb**, **Cu**, **K** (Fe, Zn, Si, Ti, Ni, Ca)	**Smalt Blue** **Cu-Zn Green**	**1.17**	**21.9**
 	Shallow bowl with design of *Grapevine*	Late Period (1653–1654)	Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, Ni, Ti, Ca)	**Cu-Zn Green**	**-**	**26.4**
 	Shallow bowl with design of *Jumokuzu (Big Tree)*	Late Period (1654–1655)	Green Enamel **Pb**, **Cu**, **K** (Si, Fe, Zn, Ni, Ti, Ca)	**Cu-Zn Green**	**-**	**29.93**
	Shard # 310 (1)	Early-to-mid 1640s	Green Enamel **Pb**, **Cu**, **Si** (Ca, Fe, K, Zn, Ni, Ti, Al)	**Cu-Zn Green**	**-**	**19.07**

Table 1. *Cont.*

Analyzed Porcelains and Ceramics	Description	Historical Period	XRF Results: Enamel Matrix and Chromophores	Identified Pigments	Co/Ni Ratio (Blue)	Cu/Zn Ratio (Green)
	Shard #493 (2)	Early-to-mid 1640s	Green Enamel **Pb**, **<u>Cu</u>**, **Si**, **K** (Fe, Ca, <u>Zn</u>, Ti, Mn, Ni, Al)	**Cu-Zn Green**	**-**	**19.76**
	Shard # 22 (3)	Early-to-mid 1640s	Green Enamel **Pb**, **<u>Cu</u>**, **K**, **Si** (Fe, Ca, <u>Zn</u>, Ni, Mn, Ti, Al)	**Cu-Zn Green**	**-**	**10.68**
	Shard # 595 (4)	1652 ca	Blue Enamel **Pb**, **Cu**, **K** (Si, <u>Fe</u>, <u>Co</u>, <u>Ni</u>, <u>As</u>, Zn, Mn, Ti, Al, Ca) Green Enamel **Pb**, **<u>Cu</u>**, **K**, **Si** (Fe, Ca, <u>Zn</u>, Ni, Ti, Mn, Al)	**Smalt Blue** **Cu-Zn Green**	**0.62**	**12.04**

Furthermore, detected matches among the analyzed materials and highly relevant features are reported and discussed in additional notes labeled *Notable Matches* and *Notable Features* found at the end of each respective section.

All Ko-Kutani masterpieces and the works by Nonomura Ninsei belong to the Collection of the Ishikawa Prefectural Museum of Art. All excavated shards have been provided by the Ishikawa Archaeological Foundation.

3.1. The Early Period (1648–1650)

3.1.1. KO-KUTANI MASTERPIECES—The Ishikawa Prefectural Museum of Art Collection

Overglaze Blue—The Smalt Connection

The XRF analysis carried out on the *Phoenix* shallow bowl (Figure 1) has revealed that the overglaze-blue decoration was developed using *Smalt*. The chromophore shows the characteristic fingerprint of the European blue material—the chemical composition Fe-Co-Ni-As with ratios of Mn/Co < 1 and As/Co between 0.35–0.50, trace to minor levels of Mn, and noticeable levels of Cu—common in 17th-century *Smalt*, and no Cr (Figure 2) [7–20].

Further confirmation of the material origin is provided by the perfect match between the chemical composition of the cobalt ore sourced from the deposits located in the proximity of Marienberg, a town in the Erzgebirge region (Saxony) founded as a miners' settlement in the early 16th century [12,21] and the element association of the blue color analyzed on the *Phoenix* bowl (Figure 2, Table 2).

Table 2. Comparison of cobalt material and blue enamel.

Element Ratio	Cobalt Ore (Marienberg)	Blue Enamel (Phoenix)
Fe/Co	0.93	1.1
Co/Ni	1.0	1.16

Figure 1. (**a**) Shallow bowl with design of *Hotei*; (**b**) shallow bowl with design of *Phoenix*. Collection of Ishikawa Prefectural Museum of Art.

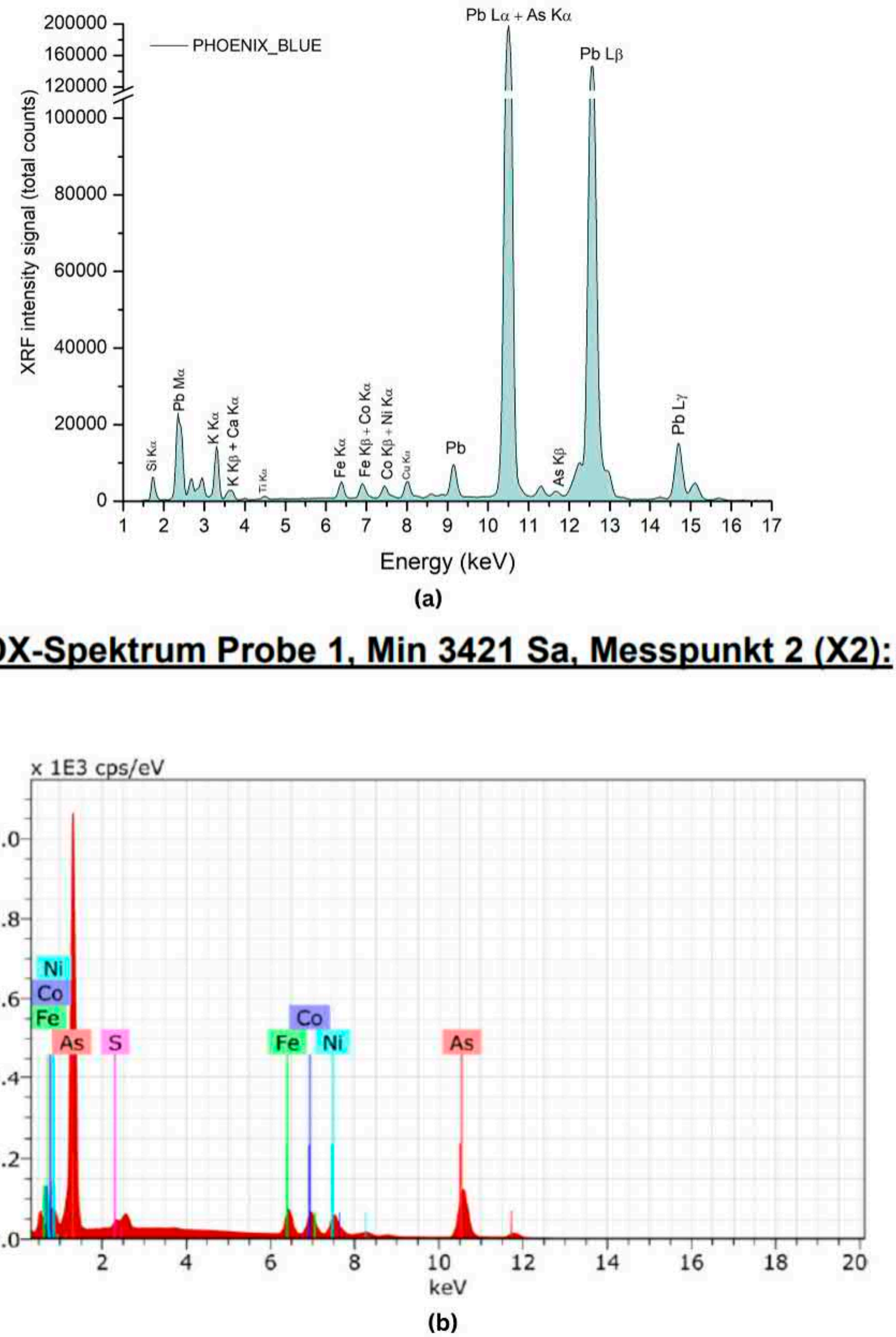


Figure 2. (**a**) XRF spectrum of the blue enamel analyzed on the *Phoenix* bowl (1648–1650); (**b**) EDS spectrum of the cobalt ore sourced from Marienberg (Erzgebirge region, Saxony) (adapted from [12]).

It is highly relevant to mention here that Japanese potters and painters will need to rely on imports of *Smalt* from Europe until the early 20th century, when Emperor Meiji's policy of strong westernization will lead to the establishment of a full-fledged state-of-the-art industry with the incorporation of preparative chemistry [7,9,22] for the industrial production of purified chemical compounds such as carbonates, sulfates, nitrates and oxides.

Overglaze Green—The Cu-Zn-As Connection

The green chromophore detected on both the *Hotei* and *Phoenix* shallow bowls (Figure 1) is characterized by the chemical composition Cu-Zn-As (Figure 3). Not only is such an element association perfectly in line with the green pigment used by the Italian painter Stefano Sparano in the 16th century [23], but it also provides a groundbreaking match with the Cu-Zn-As coloring agent identified on the folding screen *Western Kings on Horseback* painted in Japan in the early 17th century following the teachings of Giovanni Cola, the Italian Jesuit painter who established the painting *Seminario* in Japan in the early 1590s (Figure 3) [8,24].

This first-time-ever evidence helps clarifying the timeline of production of the two Ko-Kutani masterpieces: the presence of the Cu-Zn-As green on both porcelains reveals that the *Hotei* bowl, characterized by a color usage limited to green, yellow and red, preceded the *Phoenix* bowl by a matter of months. Potters had mastered the use of the Cu-Zn-As green before managing to incorporate *Smalt* as the blue chromophore. Such a novel development enabled the creation of more intricate and impactful designs, as testified by the magnificent chromatic dominance of the phoenix feathers.

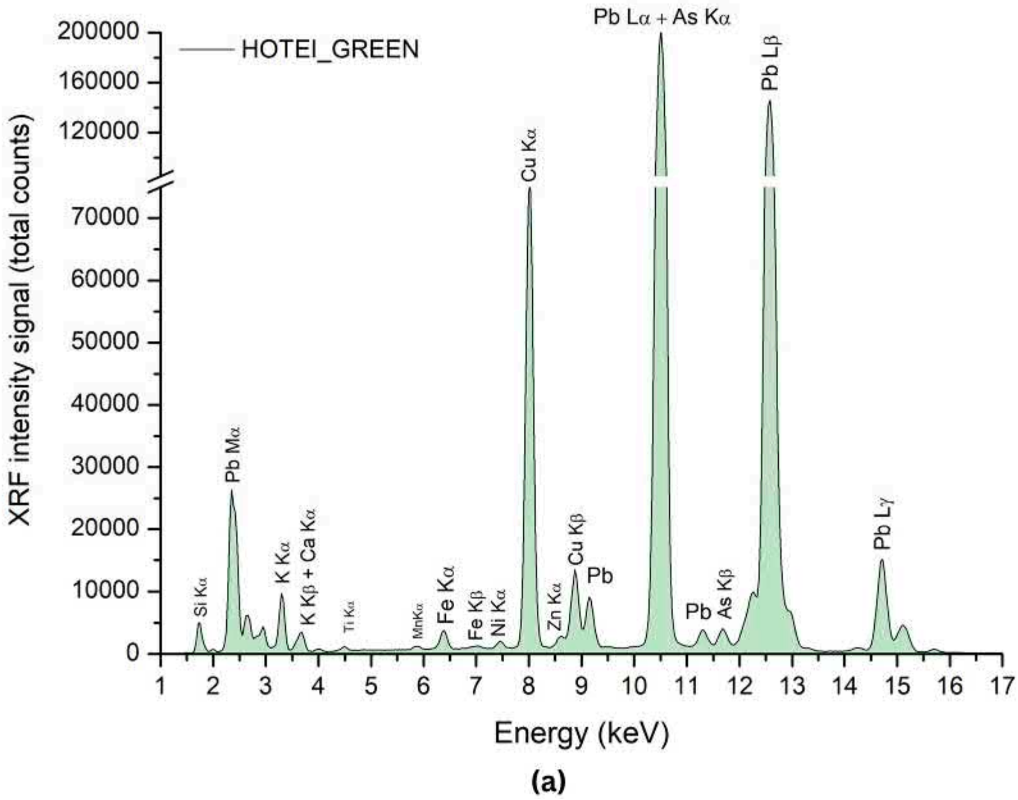


Figure 3. *Cont.*

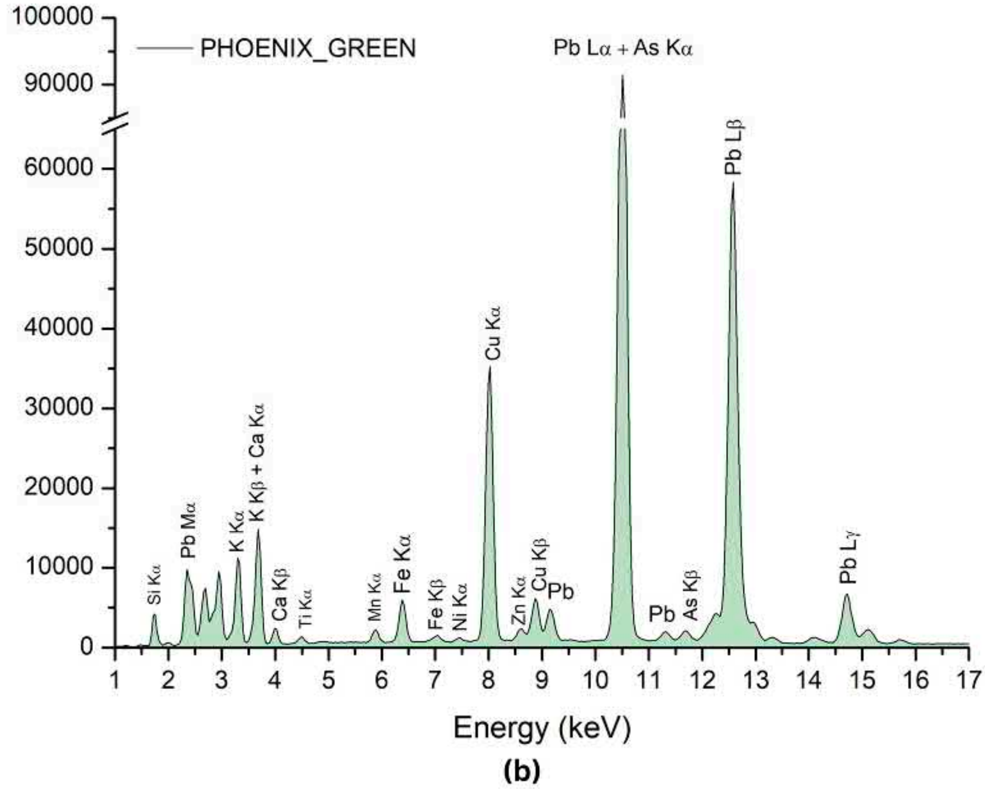


Figure 3. XRF spectra of the overglaze-green enamels bearing a Cu-Zn-As chemical composition: (**a**) *Hotei* shallow bowl; (**b**) *Phoenix* shallow bowl.

Another relevant instance consistent with our newly identified timeline comes from the decoration on the underside of the two Ko-Kutani wares: the *Hotei* bowl presents plum sprays painted in underglaze blue with overglaze-red detailing (Figure 4), while the *Phoenix* bowl bears floral scrolls in overglaze-blue enamel exclusively (Figure 4). The *Phoenix* bowl, therefore, shows a transitional feature, namely, the dominant overglaze-blue decoration on the underside, which will later mark the mature Proto-Aode style in the Middle Period (1650–1651). Such a relevant characteristic strongly points to the firing of the *Phoenix* bowl within the early months of the year 1650, while the firing of the *Hotei* bowl must consequently have occurred within the timeframe 1648–1649.

In terms of overall design composition, traditional Japanese restrained decoration and the extensive use of blank space, typical of Tawaraya Sotatsu's style in the 1630s (the painter Tawaraya Sotatsu had connections with the Maeda clan and with the renowned Kyoto Master potter Nonomura Ninsei), clearly characterize the Early Period.

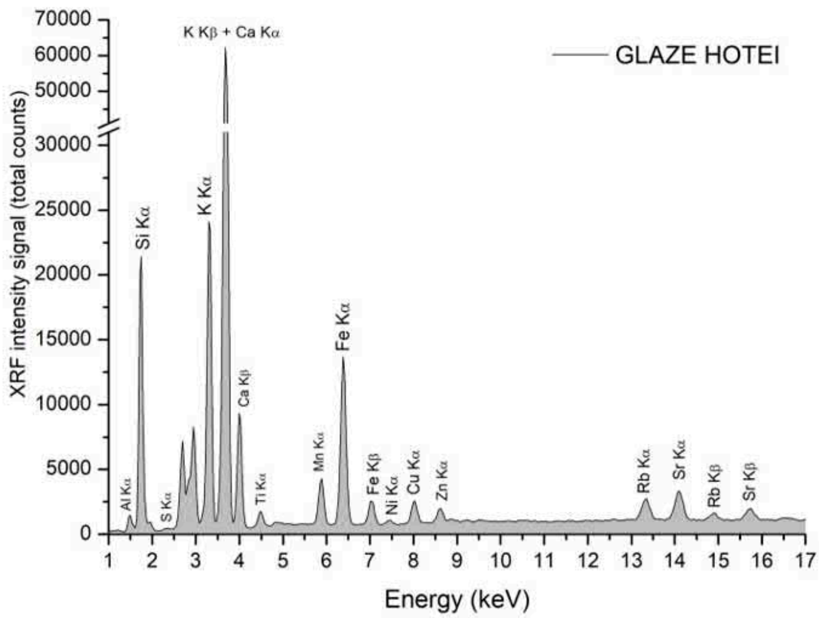
Noteworthy is that the XRF results, as expected, have confirmed the origin of the pigment used for underglaze-blue painting on all Ko-Kutani porcelains: a Mn-rich cobalt ore (Mn/Co ratios 3–4.5) with no association with As, sourced from Chinese deposits [8,9,25].

(a) (b)

Figure 4. (**a**) Underside of *Hotei* shallow bowl; (**b**) underside of *Phoenix* shallow bowl (Collection of Ishikawa Prefectural Museum of Art).

Glaze

A further crucial finding to report for this period emerged from the analysis of the glaze. XRF spectra acquired on the *Hotei* and *Phoenix* bowls (Figure 5) show how potters developed a glaze recipe aimed at exploiting the visual impact of overglaze enamels. By bringing the Rb/Sr ratio close to the value of one (0.8 and 0.91, respectively), thus aiming at a 1:1 ratio of porcelain stone to wood ash, the transparency of the glaze was greatly reduced [26,27].



(a)

Figure 5. *Cont*.

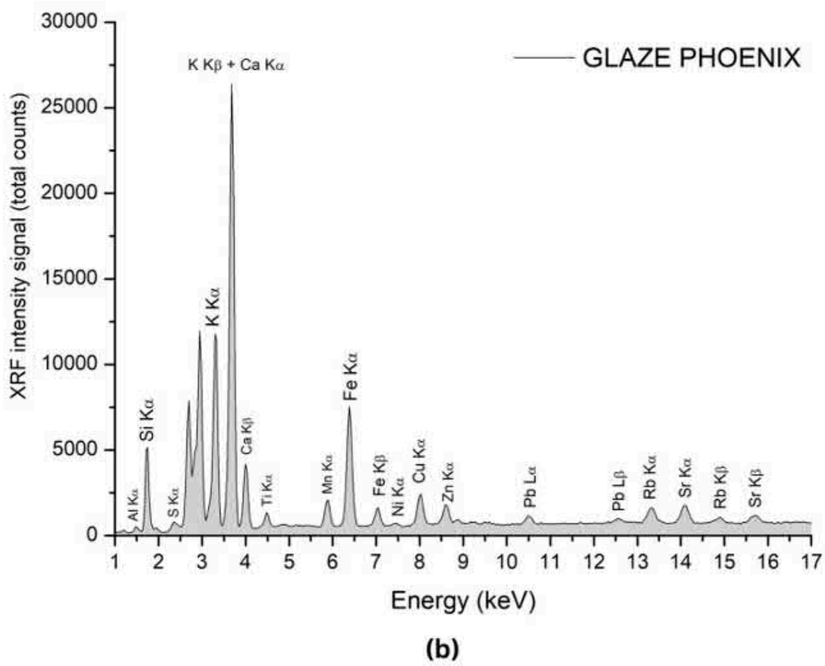


Figure 5. XRF spectra of glazes: (**a**) *Hotei* shallow bowl, Rb/Sr ratio 0.8; (**b**) *Phoenix* shallow bowl, Rb/Sr ratio 0.91.

The result was a basically subdued yet uniform white color upon which overglaze enamels would stand out, to achieve an effect much like the lead–tin opacified glazes of Europe. Further confirmation of the timeline of production comes from the calcium to potassium ratios detected on the two Ko-Kutani masterpieces: 2.6 for the *Hotei* bowl and 2.16 for the *Phoenix* bowl. The *Hotei* bowl, therefore, features a slightly more transparent glaze (a higher Ca coming from a higher content of plant ash in the glaze recipe), while the *Phoenix* bowl features a slightly more opaque glaze (a lower Ca and higher K as a result of the lower content of plant ash in the glaze recipe) [27].

Movement of Potters, Technological Transfer and Design Development

In order to fully comprehend the development of Ko-Kutani porcelain as unveiled by the evidence presented so far, let us now focus on the movement of potters in Japan in the 17th century. Records in Arita report that in March 1637, the Nabeshima clan ordered 826 potters to leave the trade [28], and that in 1647 another order was enforced by the authorities limiting the number of licenses for master potters to 155 [28]. It is important to mention here that overglaze enamels had not yet been developed in Arita at the time of the first Nabeshima decree in 1637 [29,30]. Potters affected by the orders needed to find new opportunities to make a living, and Kaga, ruled by the wealthy Maeda clan who had been focusing on culture as a survival strategy in the tense relationship with the Tokugawa shogunate, was a very promising place. In addition, the Maeda fiefdom had become a thriving center of cultural exchange between Japan and Europe [31,32], considering that the Christian samurai Takayama Ukon and Naito Tokuan Johan had settled there in the early 1600s, before the enforcement of the fierce persecutions by the Tokugawa shogunate in 1614 following the ban on Christianity [32]. In particular, Naito Tokuan Johan had provided the necessary patronage for the establishment of the first Jesuit glass workshop in the Far East by the Italian Jesuit painter Giovanni Cola in Arie (Kyushu) in 1595 [31], thus being directly involved in the development of enamels and painting pigments such as *Smalt* under the supervision of Giovanni Cola himself, and witnessing the transfer of technology from Italy to Arie in the late 16th century [33,34].

3.1.2. Nonomura Ninsei: Early Materials and Techniques (1648–1650)—Connections and Influences in Kaga (1640s)

Archaeological excavations at the *Noborigama* (climbing kiln for high firing) kiln site in Kaga have provided compelling evidence of the presence of the Kyoto master potter Nonomura Ninsei in the Maeda fiefdom in the latter half of the 1640s. Specifically, the unearthed shard of a Ko-Kutani *sometsuke* (blue and white) bowl (Figure 6) has unveiled the origin of the iconic plum design that adorned Ninsei's celebrated tea ceremony wares (Figure 6). The implication is clear: Kaga potters exerted a strong influence on the stylistic development of Ninsei's ceramics way before the establishment of the Kyoto kiln in 1648. Moreover, written records report that the Lord of the Maeda fiefdom acquired valuable tea ceremony vessels from Nonomura Ninsei through the mediation of the tea master Kanamori Sowa (1584–1656), thus providing a continued link between Kaga and Kyoto [35,36].

It has therefore become crucial to determine whether the Kaga potters' influence also involved the transfer of European materials and technology to Kyoto. In order to investigate such a relevant possibility and uncover an unknown dynamic, three major works by Nonomura Ninsei (Collection of Ishikawa Prefectural Museum of Art) have been analyzed by XRF. The results are reported in the sections below. Additional notes regarding some of the most relevant materials are labeled *Notable Matches*.

Figure 6. (**a**) Shard of a blue-and-white Ko-Kutani bowl bearing the iconic plum design, latter half of the 1640s, excavated at Kaga Kutani kiln site 1 (Collection of Ishikawa Archaeological Foundation);

(**b**) detail of decoration on Nonomura Ninsei's *Mizusashi* (Water Jar) (Important Cultural Property of Japan); (**c**) detail of decoration on Nonomura Ninsei's *Mizusashi* (Water Jar) (Important Cultural Property of Japan). Collection of Ishikawa Prefectural Museum of Art.

Overglaze Blue—The Smalt Connection

XRF analysis has proven, for the first time ever, that Nonomura Ninsei used the European blue pigment *Smalt* for the overglaze decoration of the Incense Burner in the Shape of a Pheasant (*Koro*) and the Incense Container (*Kogo*) (Figures 7 and 8). The chromophore, as observed on the Phoenix bowl, shows the distinctive fingerprint of the European blue material—the chemical composition Fe-Co-Ni-As with ratios of Mn/Co < 1 and As/Co between 0.35–0.50, trace to minor levels of Mn, no Cr, and noticeable levels of Cu—common in 17th-century *Smalt* [7–20].

Such a crucial discovery firmly links the Kaga potters' characteristic practice of using *Smalt* for overglaze-blue enameling on Ko-Kutani porcelains to the development of Ninsei's style of decoration. All XRF spectra, consistently and conclusively, identify Europe as the source of the blue coloring agent employed on both the Ko-Kutani masterpieces and Ninsei's works. The early and successful use of the imported pigment clearly implies that Ninsei must have learnt European enameling technology during his stay in Kaga under the supervision of *Seminario* graduates before the establishment of his own kiln in Kyoto in 1648, thus placing the firing of the Incense Burner in the Shape of a Pheasant (*Koro*) (National Treasure) in the timeframe 1648–1650.

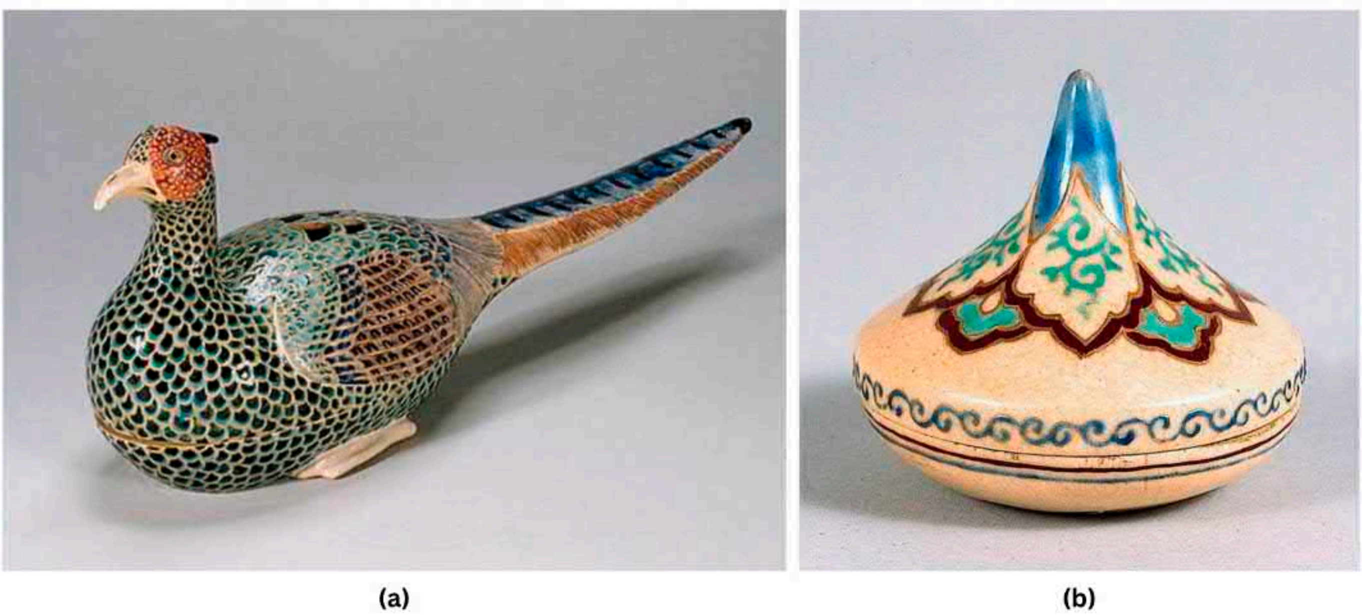


Figure 7. (**a**) Nonomura Ninsei's Incense Burner in the Shape of a Pheasant (*Koro*) (National Treasure); (**b**) Nonomura Ninsei's Incense Container (*Kogo*). Collection of Ishikawa Prefectural Museum of Art.

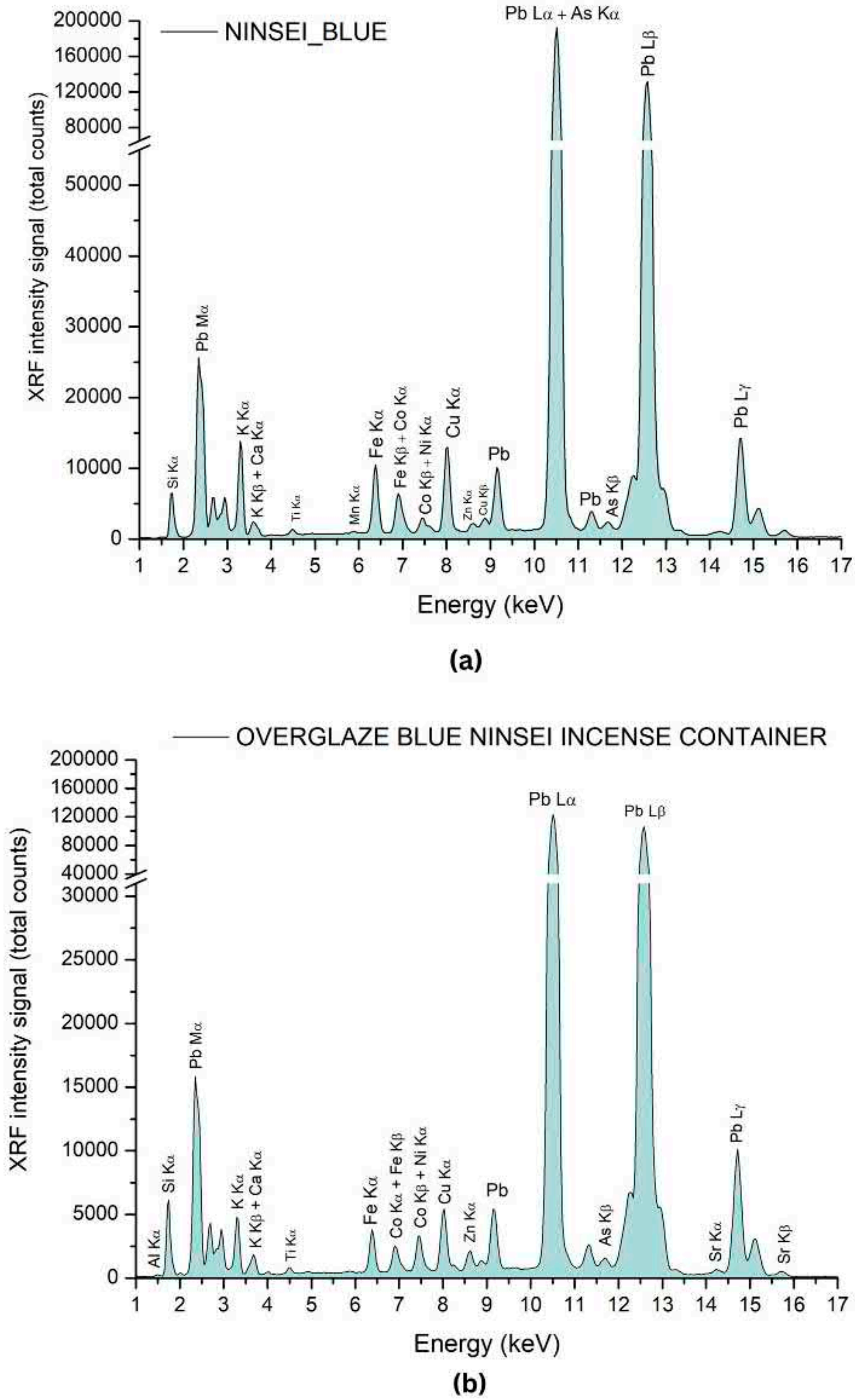


Figure 8. Nonomura Ninsei: (**a**) Incense Burner in the Shape of a Pheasant—XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**b**) Incense Container (*Kogo*)—XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content).

Notable Features: Blue Enamel

Furthermore, a very interesting instance emerges from the cobalt to nickel ratios detected on the Incense Burner in the Shape of a Pheasant (*Koro*, 1648–1650) (Co/Ni ratio of 2.15) and the Incense Container (*Kogo*, fired after 1650) (Co/Ni ratio of 0.76). Ninsei appears to have used an overglaze-blue enamel richer in cobalt in the earliest production phase in Kyoto (1648–1650). Here, history comes into play and provides the explanation for the scientific finding: the Incense Burner in the Shape of a Pheasant had been originally ordered by the Maeda clan as a memorial piece for the restoration of Ninnaji temple in Kyoto in 1646 [36]. Ninsei, therefore, in order to accomplish such a demanding task needed to rely on the most refined materials he could obtain at the time. Later, as the production became more standardized to suit the needs of a wider audience, a shift to a blue material richer in nickel (less pure) took place after 1650.

This first-time-ever evidence is perfectly in line with both the variability resulting from the varying amounts of Fe, Co and Ni in the cobalt ores sourced from the large deposits in the Erzgebirge region (Saxony) and Bohemia, as by historical records and geochemical data [7–21,25,37,38], and the employment of different processing methods. Thus, it may provide a potential marker to date the works of the Master.

Overglaze Green—The Cu-Zn Connection

XRF analysis has identified a chromophore characterized by the Cu-Zn element association as the material of choice for the green enamel (Figure 9). The coloring agent bears a Cu/Zn ratio of 6.7 and provides a groundbreaking match with the European Cu-Zn-based pigment, with a Cu/Zn ratio of 6.32, detected on Emanuel Pereira's portrait of the Jesuit Father Matteo Ricci SJ (1610) (Figure 10) [33]. In particular, such a European pigment has been identified as having been used on Pereira's painting as a mixture with carbon black to provide depth to the black robe (Figure 10) [33]. That skilled application, unknown in Japan at the time, originated from the transfer of the distinctive shadowing and modeling techniques employed by painters in Renaissance Europe since the 15th century to Japanese artists [33,34].

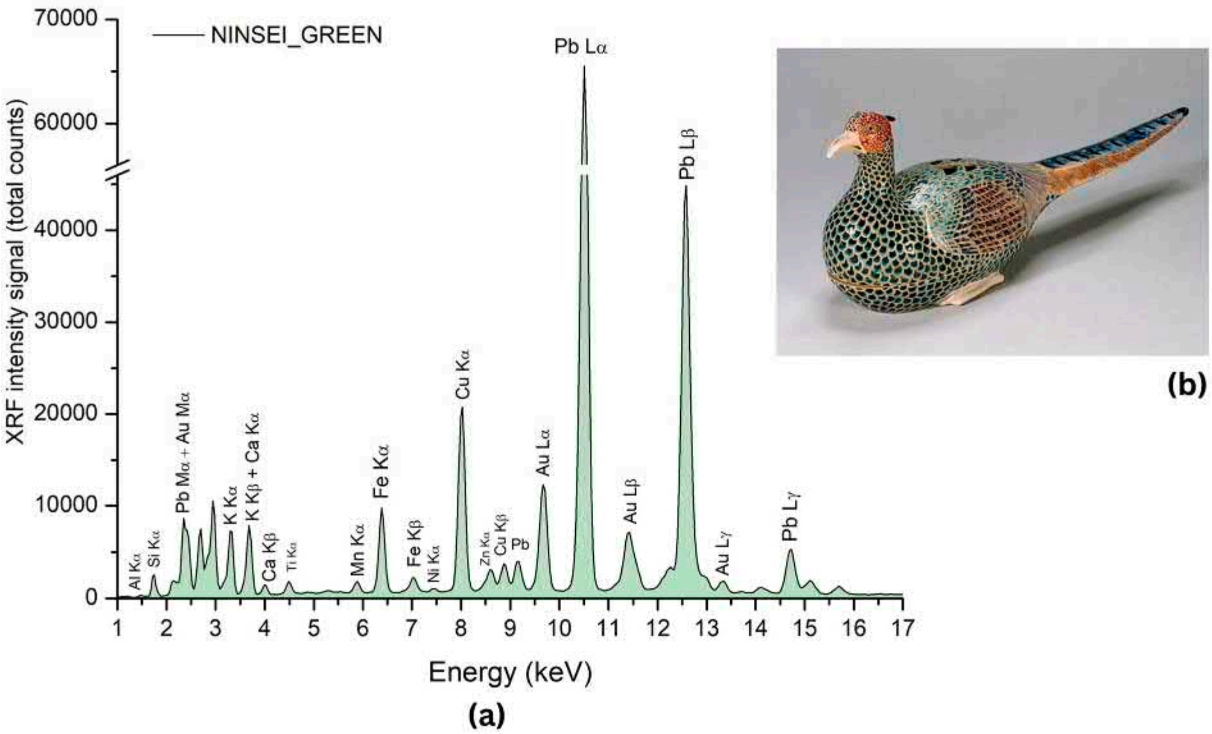
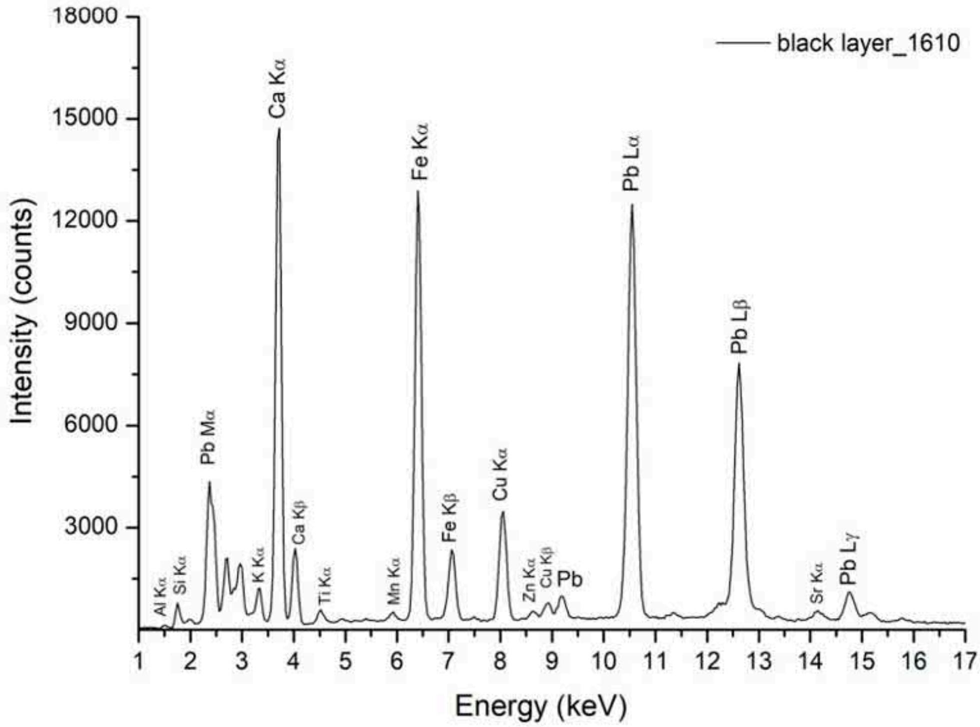


Figure 9. (**a**) XRF spectrum of overglaze-green enamel (Cu-Zn chemical composition); (**b**) Nonomura Ninsei, Incense burner in the Shape of a Pheasant (National Treasure) (Collection of Ishikawa Prefectural Museum of Art).

This first-time-ever evidence shows how the Jesuit painting *Seminario* established by the Italian Jesuit painter Giovanni Cola in the early 1590s [33,34] exerted a deep influence on both the Kaga potters and Nonomura Ninesi in the first half of the 17th century, thus revealing the extent of the technological development the Maeda clan had brought to life in the early Edo period (1603–1868).



(a)

(b)

Figure 10. (**a**) XRF spectrum of the Cu-Zn-based black pigment (*Arie Black*) identified on the portrait of Father Matteo Ricci SJ (1610); (**b**) Emanuel Pereira's portrait of Father Matteo Ricci SJ (1610) (Collection of Chiesa del Santissimo Nome di Gesù all'Argentina, Rome, Italy).

Further first-time-ever evidence to report here is provided by the analysis of the Water Jar (*Mizusashi*) (Figure 6b,c) and Incense Container (*Kogo*) (Figure 7b): XRF spectra of the green enamels reported in Figure 11 confirm that the Cu-Zn chromophore was Ninsei's pigment of choice for green enameling.

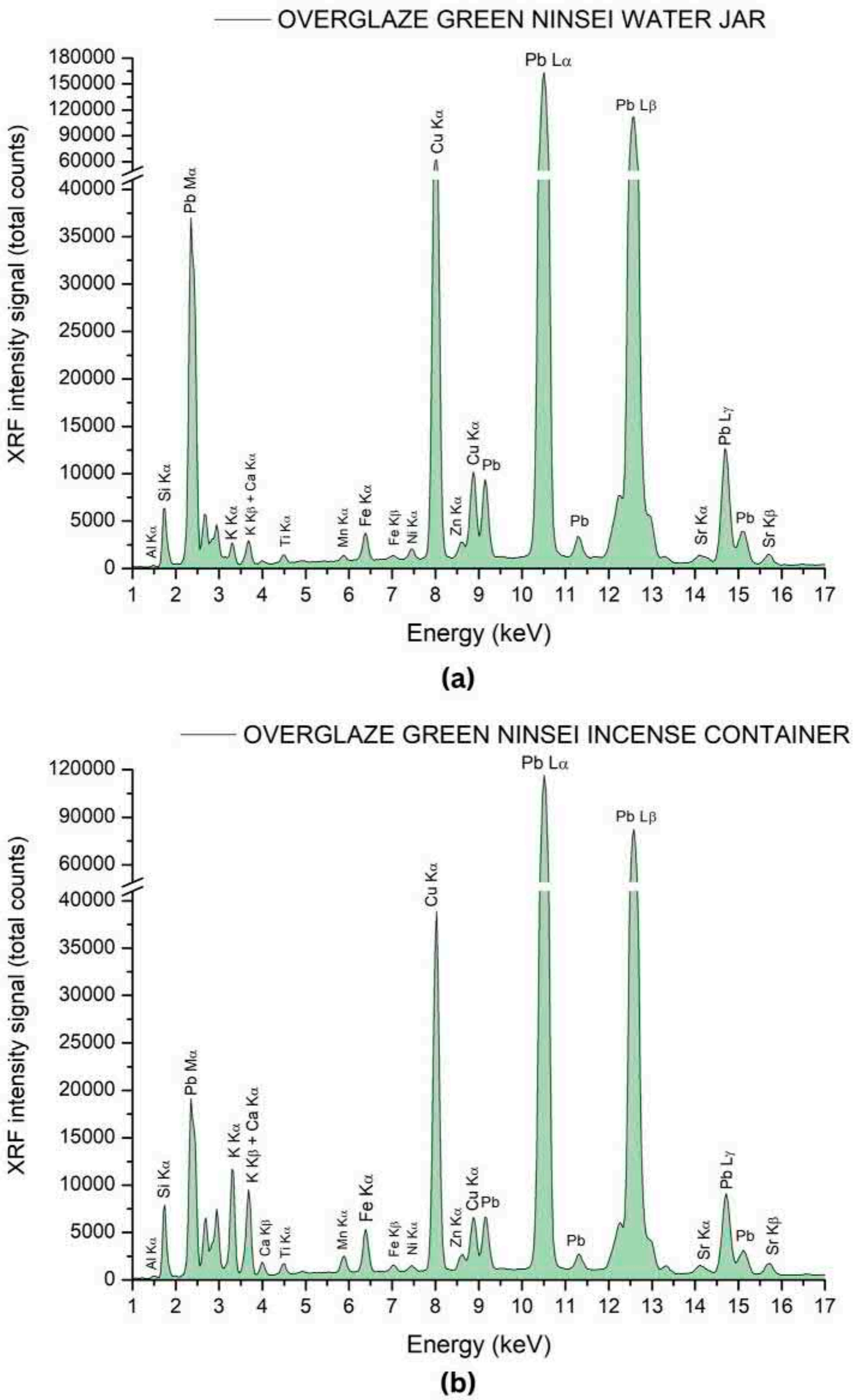


Figure 11. Nonomura Ninsei: (**a**) XRF spectrum of the overglaze-green enamel (Cu-Zn) detected on the *Mizusashi* (Water Jar); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn) detected on the Incense Container. Collection of Ishikawa Prefectural Museum of Art.

The scientific results, in accordance with the above-mentioned archaeological evidence, suggest a later timeframe for the firing of the two vessels, specifically after 1650.

Notable Matches: Green Enamel and Pigment

Also groundbreaking is the further match provided by the XRF spectra of the Cu-Zn-based green enamels analyzed on Ninsei's Water Jar (*Mizusashi*) (Cu/Zn ratio of 22.3), an Italian majolica dish fired at Deruta in the early 17th century (Saint figure) (Cu/Zn ratio of 23.9), and the green pigment detected on the Western-style painting *Martyrdom of Leonardo Kimura* painted in Japan in 1619 (Cu/Zn ratio of 23.9) (measurement point #P13 as indicated in the XRF spectrum) (Figures 12 and 13). All Cu/Zn ratios fall into a consistent range of values (chart reported in Figure 12): this first-time-ever evidence, as for the case of Ninsei's Incense Burner in the Shape of a Pheasant (*Koro*), is exceptionally important considering both the distant geographical areas involved and the different supports upon which the Cu-Zn-based green materials have been applied. The transfer of European technology and materials to Kaga and their strong influence on Ninsei's development of overglaze enameling in Kyoto has therefore been firmly proven once again.

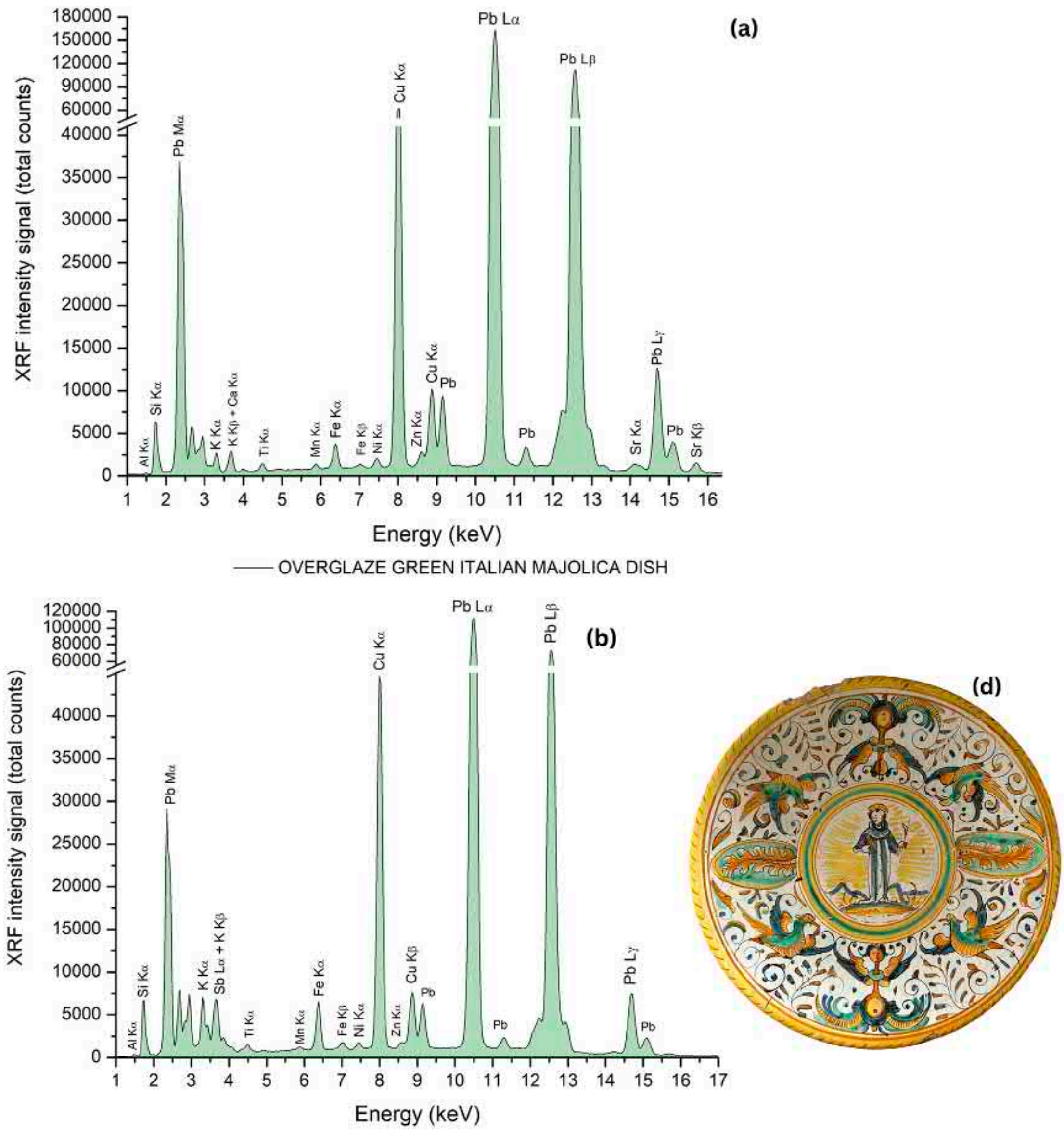


Figure 12. *Cont.*

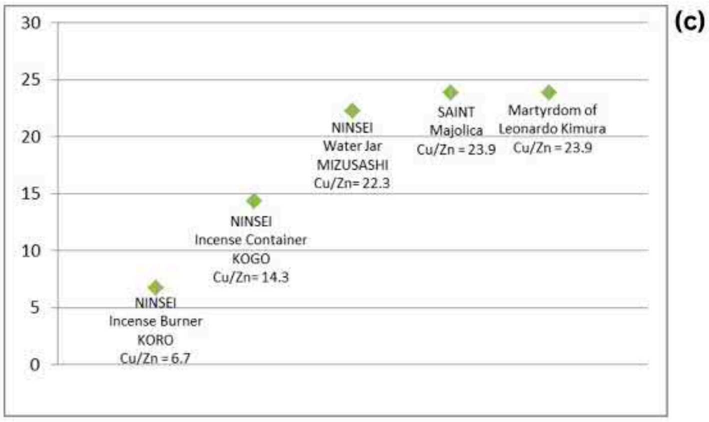


Figure 12. (**a**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition) analyzed on Ninsei's Water Jar (*Mizusashi*); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition) detected on the early-17th century Italian majolica dish (Saint); (**c**) chart with Cu/Zn ratios for the green enamels analyzed on Ninsei's wares, the Saint majolica dish and the *Martyrdom of Leonardo Kimura* (1619); (**d**) early-17th century Italian majolica dish (Saint) (private collection).

Moreover, the chart in Figure 12 suggests that, as previously discussed for the blue enamel, Ninsei carried out an extensive experimentation aimed at devising recipes that would fit the decoration on his wares best. In particular, the Cu/Zn ratios of 6.7 for the Incense Burner (*Koro*), 14.3 for the Incense Container (*Kogo*) and 22.3 for the Water Jar (*Mizusashi*) (chart in Figure 12) indicate that the earliest wares were decorated with a more opaque and glossier green (richer in zinc), while after 1650 (the firing of the Incense Container and Water Jar) a more standardized production process was progressively implemented: the Cu/Zn ratio on the Water Jar reaches 22.3 and settles in the range of values belonging to the ready-to-use pigments of European origin detected on the Italian majolica dish (Saint) and the *Martyrdom of Leonardo Kimura* (chart in Figure 12), both bearing an identical Cu/Zn ratio of 23.9.

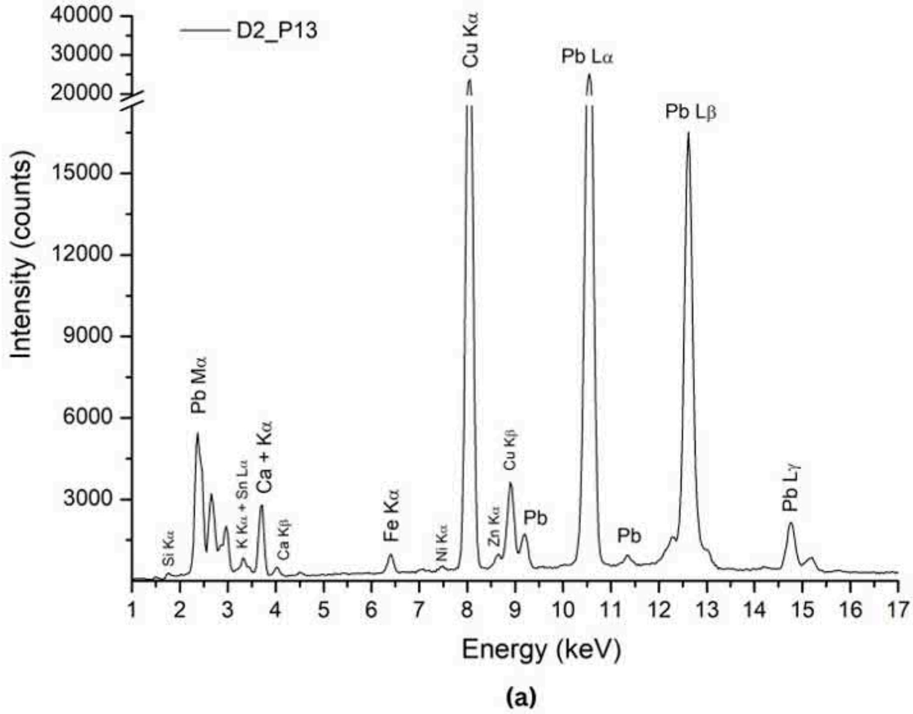


Figure 13. *Cont.*

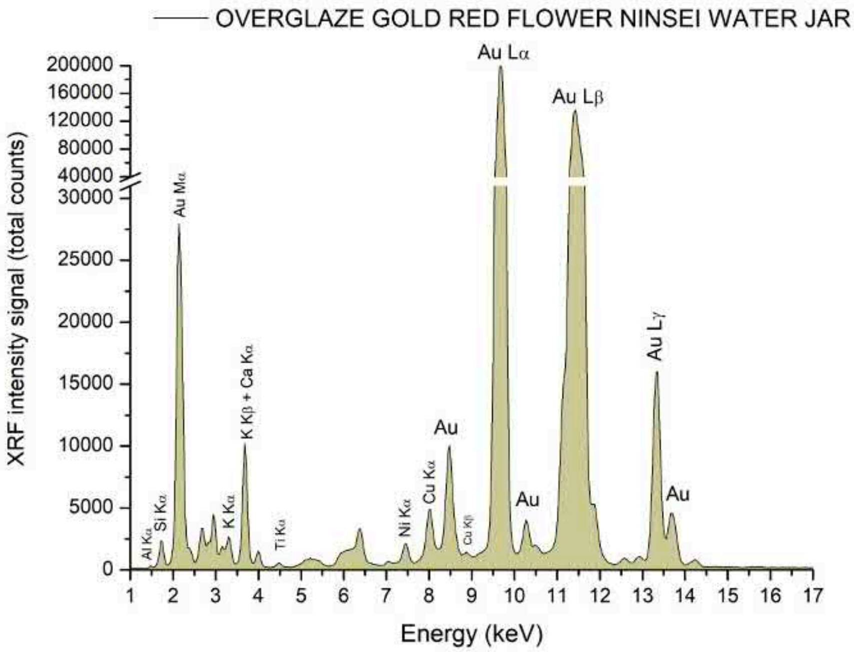
(b)

Figure 13. (**a**) XRF spectrum of the overglaze-green enamel, Cu-Zn chemical composition with a Cu/Zn ratio of 23.9, detected on the *Martyrdom of Leonardo Kimura*; (**b**) Western-style Japanese painting depicting the *Martyrdom of Leonardo Kimura* (1619) (Collection of Chiesa del Santissimo Nome di Gesù all'Argentina, Rome, Italy).

Gold Paint Application on Ceramics: Nonomura Ninsei's Groundbreaking Innovation

The Water Jar (*Mizusashi*) (Figures 11 and 14), fired by Ninsei in Kyoto, is characterized by a decoration technique that would influence Japanese porcelain production for centuries to come. XRF analysis has revealed that gold outlining and detailing were obtained by the cold application of a gold paint/foil to the already high-fired and enameled body (Figures 14 and 15). This distinctive innovation introduced by Ninsei has been detected and identified for the first time ever in the present work.

The origin of such a decoration style can be easily identified in the Italian painting technique, dating back to the 14th century [39–44], extensively applied on Western-style paintings and screens produced in Japan under the supervision of Jesuit Missionaries from the late 16th century onward. Both the *Western Kings on Horseback Screens* (Suntory Museum of Art; Kobe City Museum, early 17th century) and the *Jesuit Martyrs in Japan* (Macau, 1630s) (Figure 15) widely feature it [24,33].



(a)

(b)

Figure 14. Nonomura Ninsei's *Mizusahsi* (Water Jar for the tea ceremony): (**a**) XRF spectrum of the gold decoration; (**b**) detail of gold decoration. Collection of Ishikawa Prefectural Museum of Art.

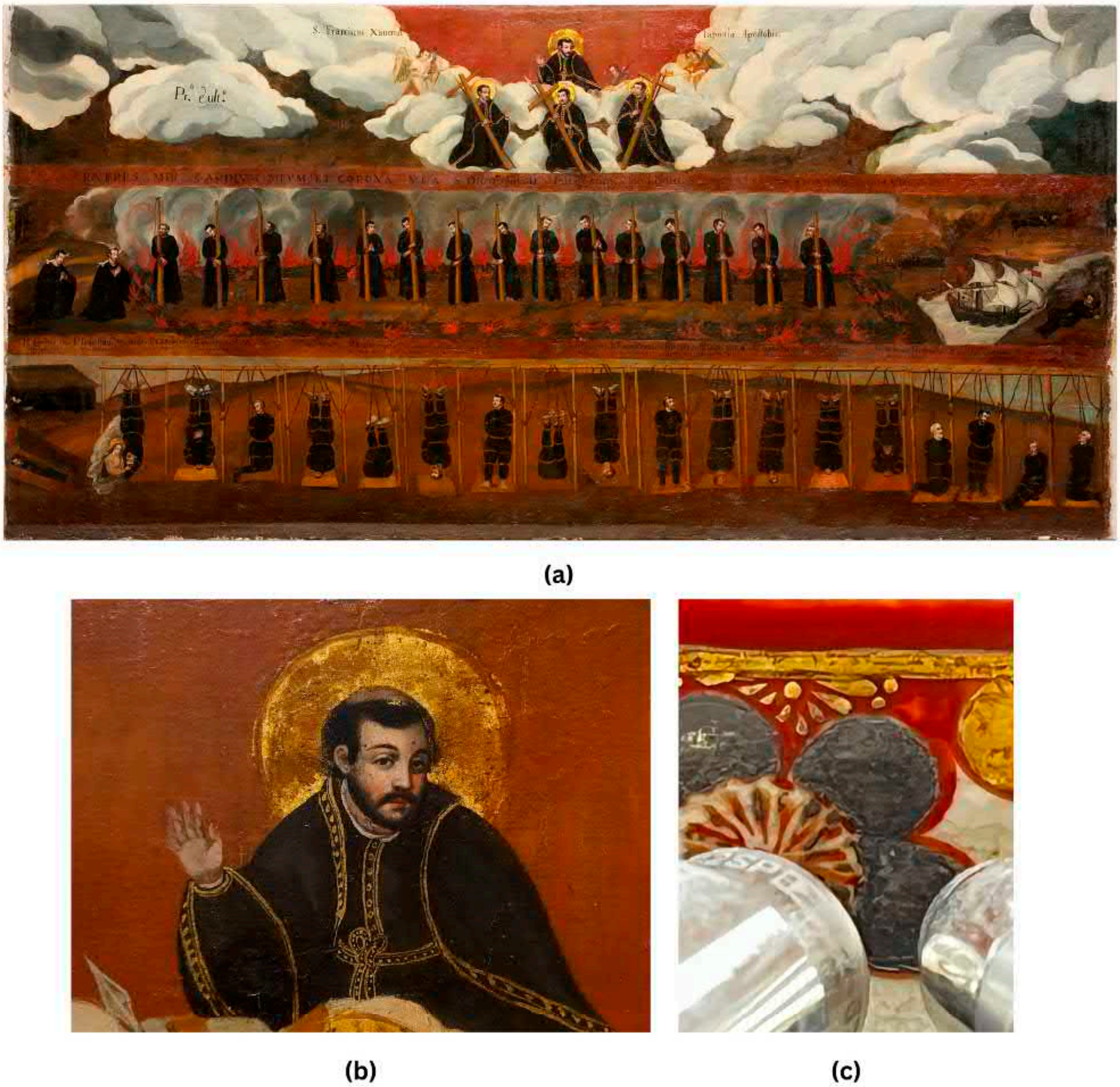


Figure 15. (**a**) European-style painting *Jesuit Martyrs in Japan*, 1630s (Collection of Chiesa del Santissimo Nome di Gesù all'Argentina, Rome, Italy); (**b**) detail of gold decoration on the *Jesuit Martyrs in Japan*; (**c**) detail of gold decoration on the *Mizusashi* (Water Jar) by Ninsei (Collection of Ishikawa Prefectural Museum of Art).

This novel and groundbreaking evidence reveals how, as in the case of the Cu-Zn green (Section 3.1.2), Jacob Niwa and other Japanese and Chinese painters who had trained under Giovanni Cola, the Italian Jesuit painter who established the painting *Seminario* and glass workshop in Arie (Kyushu) in 1595, incorporated innovative European techniques as a result of Cola's teaching [33], and that these innovations spread to other Japanese art circles, as testified by Ninsei's wares and the use of *Smalt* on Buddhist works of art from the late 16th century onward [7,45,46].

Ninsei, therefore, had clearly been exposed to European artistic practices in a thriving environment of cultural and technical exchange. History, as in the case of the Incense Burner in the Shape of a Pheasant, provides the circumstances that led to the inception of the decoration style by the Master: Maeda Toshitsune (Third Lord of the Maeda clan) had ordered the Kyoto lacquer artist Igarashi Doho to establish a lacquer workshop in the Kaga domain. The earliest result of such an artistic endeavor was the lacquer *maki-e* box (for the storage of sacred scriptures) created by Igarashi Doho himself and donated to Daihonzan Hokkekyo-ji Temple in 1646 [47]. The development of the novel cold gilding style on ceramics proves the result of Ninsei's assimilation of both European and Japanese techniques. Its inception can be consistently and safely placed within the latter half of the 1640s, and must have reached its final form before the establishment of the Kyoto kiln in 1648, where it was perfected as observed on the *Mizusashi* (Water Jar).

3.2. The Middle Period (1650–1651)

3.2.1. KO-KUTANI MASTERPIECES—The Middle Period and the Proto-Aode Style (1650–1651)

The Middle Period is characterized by the introduction of a new and groundbreaking decoration technique. Specifically, the gradual and steady decrease in the blank space that had marked the restrained compositional approach of the Early Period would lead to the establishment of the Proto-Aode style. Such a novel decoration scheme would be characterized by the practice of extensively covering the front of the bodies with enamels, and systematically replacing underglaze-blue motifs with overglaze colors on the underside, with only some parts left undecorated (Figures 16–27).

XRF analysis has revealed that potters, with uninterrupted consistency, gave birth to this stylistic transition by relying on the same materials they had been using since the Early Period: European *Smalt* for overglaze-blue decoration and the Cu-Zn-As coloring agent for the green color. The Ko-Kutani tradition had finally established its strong, distinctive and iconic roots.

Underglaze-blue painting, after a short-lived continuation, would be gradually replaced by overglaze-enameled motifs. The XRF results confirm that the cobalt ore used for underglaze-blue painting was sourced from Chinese deposits.

Materials and Techniques

The Ko-Kutani porcelains belonging to the Middle Period are listed in the order of their firing, from earliest to latest. The development of the decoration schemes and motifs, along with their associated materials, can be clearly identified and dated. Spectra of the overglaze-blue and overglaze-green enamels are reported for each example, where present. Additional notes regarding some of the most relevant materials and stylistic features are labeled *Notable Matches* and *Notable Features*. The yellow color and glaze will be discussed in Sections 3.6.3 and 3.8, respectively.

Shallow Bowl with Scattered Treasures and Heron Design (1650–1651)

Notable Features: Decoration Style and Green Enamel

The *Scattered Treasures and Heron* bowl (Figure 16) represents the transition from the Early Period to the Middle Period. Apart from the appearance of the newly developed Proto-Aode style, based on a richer and broader decoration of the front, the bowl still retains some stylistic features of the previous period. In particular, the restrained motifs applied on the basically plain underside, as seen on the *Hotei* bowl (Section 3.1.1—Figure 4), are painted here in overglaze enamels, following the style introduced on the *Phoenix* bowl (Section 3.1.1—Figure 4). Extremely relevant is the first-time-ever identification of the main technological connection between the two periods: the continued use of the Cu-Zn-As-based green enamel.

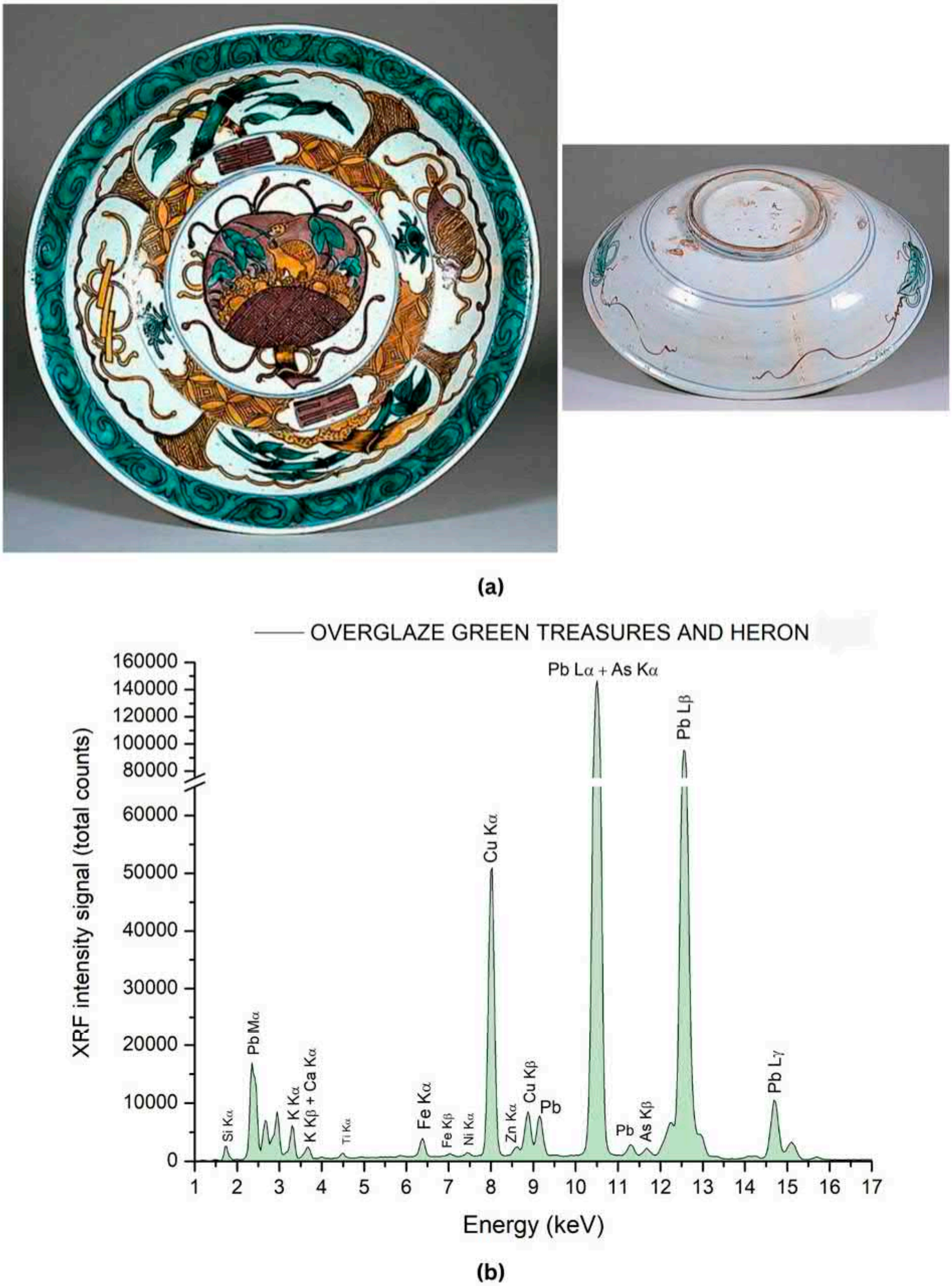


Figure 16. Shallow bowl with *Scattered Treasures and Heron* design: (**a**) front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel bearing a Cu-Zn-As chemical composition.

Shallow Bowl with *Quail* Design (1650–1651)

Notable Features: Green and Blue Enamels

A remarkable confirmation of the firing timeline identified for the *Hotei* and *Phoenix* bowls in the Early Period (Section 3.1.1) comes from the detection on the *Quail* bowl of both the Cu-Zn-As-based green enamel and the *Smalt*-based blue enamel (Figure 17): Kaga potters continued to adhere to the initial practice of firing wares bearing the Cu-Zn-As green first, as in the case of the *Hotei* bowl in the Early Period (Section 3.1.1) and the *Scattered Treasures and Heron* bowl in the Middle Period, to then add to the complexity of the design by also employing the *Smalt*-based blue enamel in a further step, as in the case of the *Phoenix* and *Quail* bowls that bear both. A technological standardization had clearly matured and taken root.

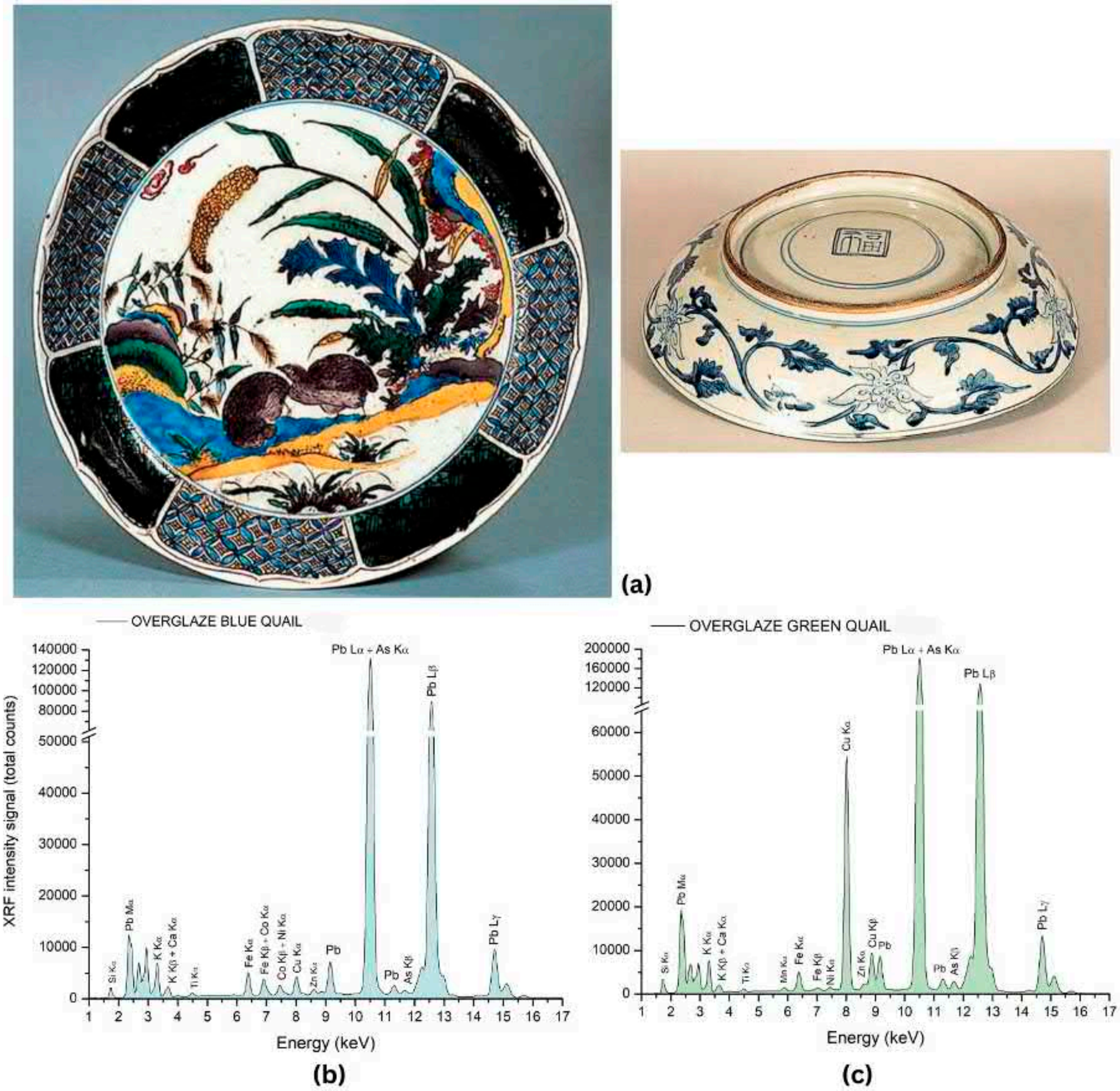
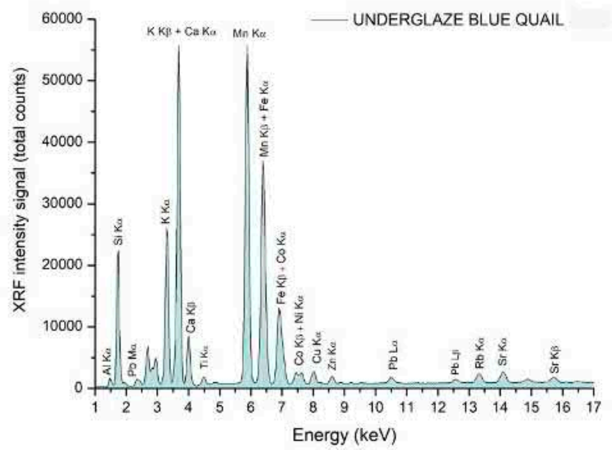


Figure 17. *Cont*.



(d)

Figure 17. Shallow bowl with *Quail* design: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**d**) XRF spectrum of the underglaze-blue pigment.

Shallow Bowl with *Paving Stone Pattern* (1650–1651)

Notable Matches: Blue Enamel and Pigment

Extremely relevant is the match between the overglaze-blue enamels analyzed on the *Paving Stone Pattern* (Co/Ni ratio of 1.6) and *Quail* (Co/Ni ratio of 1.52) bowls (Figures 18 and 19): this first-time-ever evidence provides a further testimony to the continued technological influence exerted by European *Smalt* on Ko-Kutani overglaze-blue enameling. *Smalt* proves to be the fundamental material upon which the iconic roots of Ko-Kutani porcelains were based since their first inception.

Moreover, also striking is the perfect consistency of the Chinese cobalt-based pigment used for underglaze-blue decoration on the two bowls: the identical XRF spectra are characterized by an identical Mn/Co ratio of 4.2 (Figure 19).

(a)

Figure 18. *Cont.*

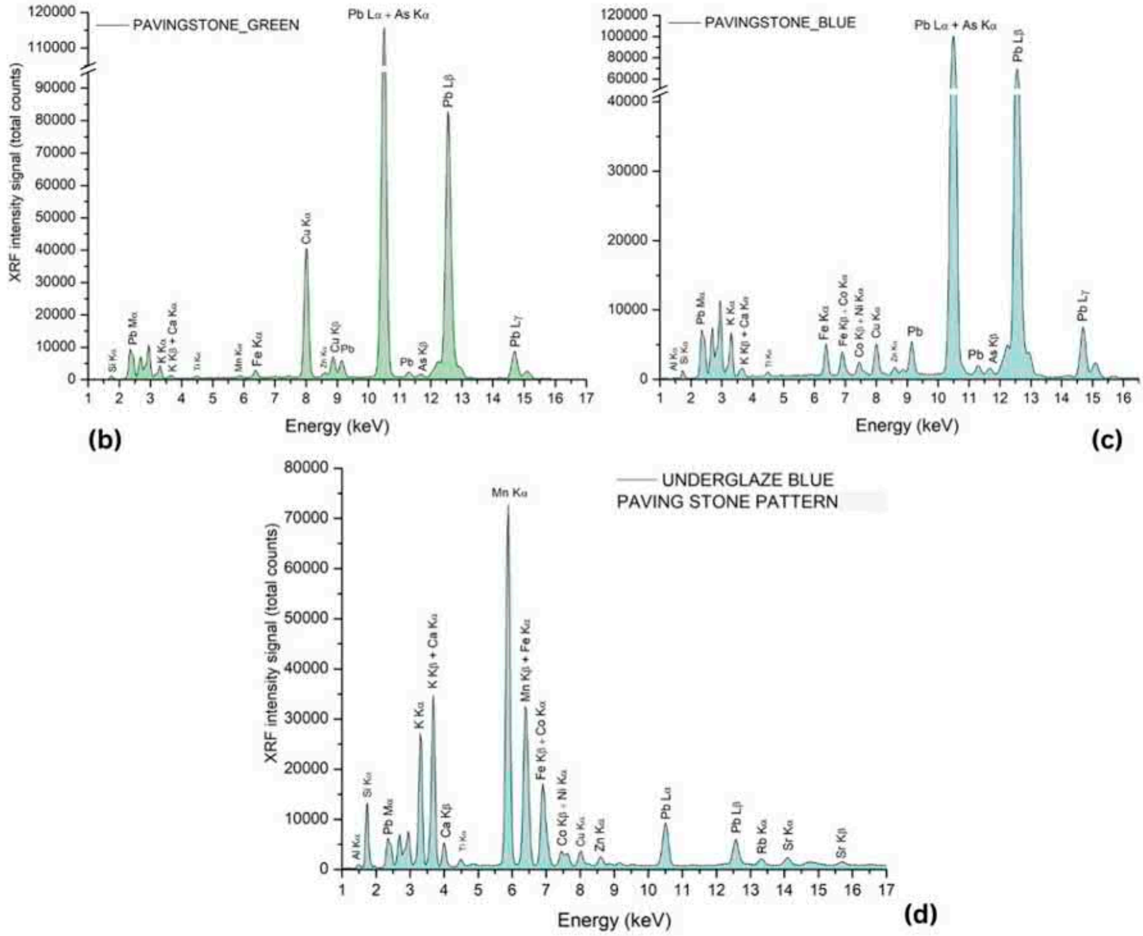


Figure 18. Shallow bowl with *Paving Stone Pattern* design: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**d**) XRF spectrum of the underglaze-blue pigment.

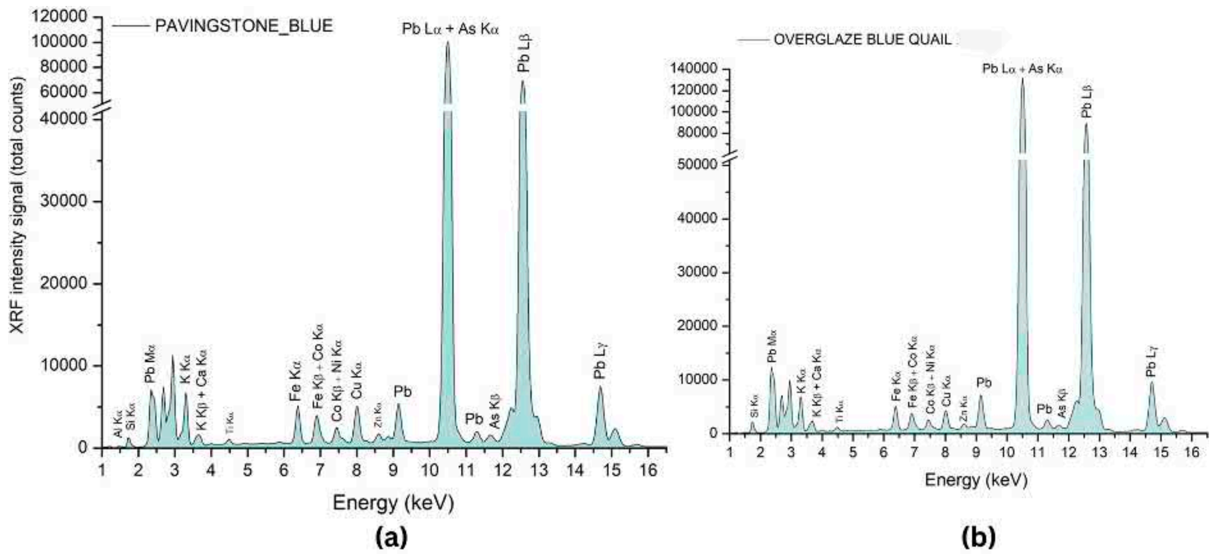


Figure 19. *Cont.*

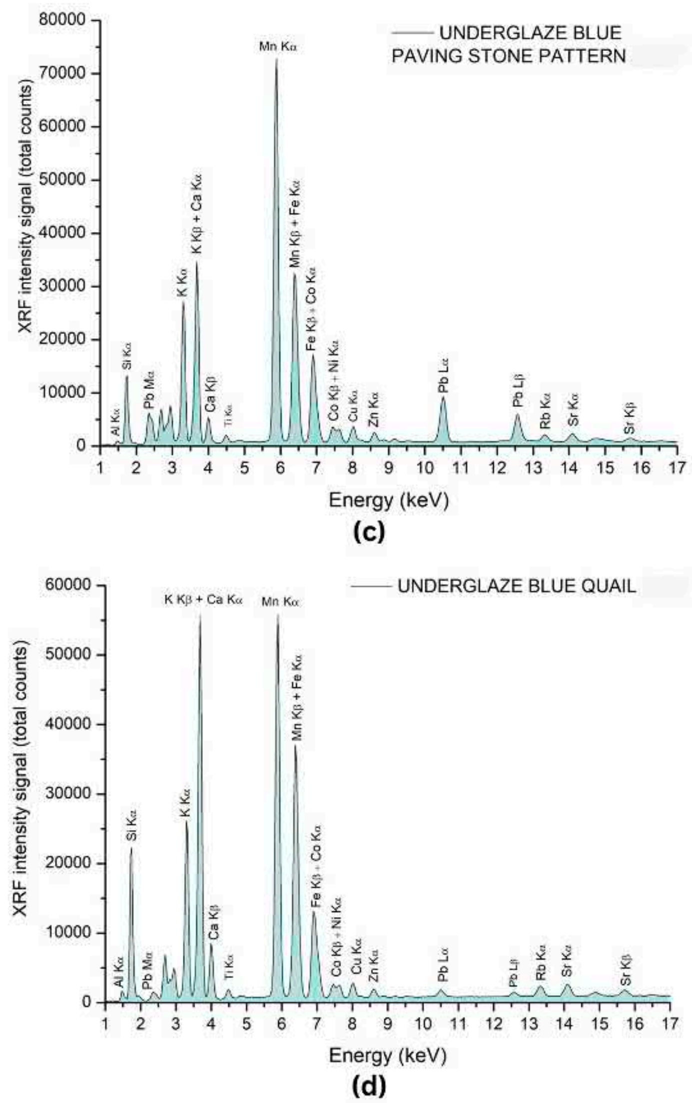


Figure 19. (**a**) XRF spectrum of the overglaze-blue enamel detected on the *Paving Stone Pattern* bowl (Fe-Co-Ni-As chemical composition with high K content); (**b**) XRF spectrum of the overglaze-blue enamel analyzed on the *Quail* bowl (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the underglaze-blue pigment analyzed on the *Paving Stone Pattern* bowl (Mn/Co ratio 4.2); (**d**) XRF spectrum of the underglaze-blue pigment analyzed on the bowl with *Quail* design (Mn/Co ratio 4.2).

Shallow Bowl with Design of *Peonies in Overglaze Enamels* (*Iro-e Botan*) (1650–1651)

Notable Features: Decoration Style and Green Enamel

The decoration on the underside of the *Peonies in Overglaze Enamels* (*Iro-e Botan*) bowl (Figure 20) shows the complete replacement of the underglaze-blue pigment with overglaze enamels. This shift proves to be a fundamental step as it unveils the ongoing development of the Full Aode style. Moreover, the green enamel proves consistent, once again, with the material of choice for the green decoration in the Middle Period, that is, the Cu-Zn-As-based chromophore.

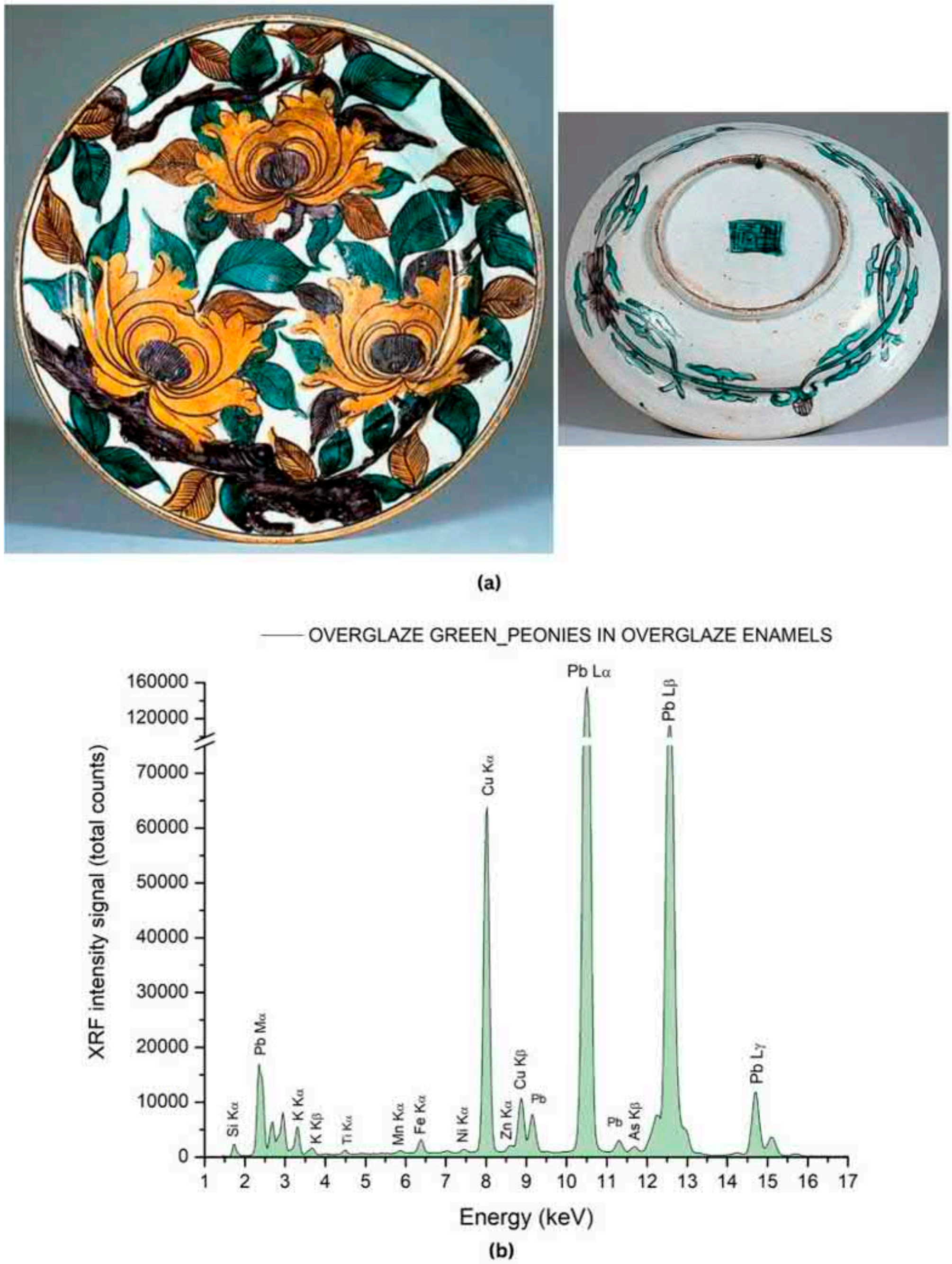


Figure 20. Shallow bowl with design of *Peonies in Overglaze Enamels (Iro-e Botan)*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition).

Shallow Bowl with Design of *Flowers and Bird Inside Jar* (1650–1651)

Notable Matches: Blue and Green Enamels

It is relevant is to remark here the first-time-ever evidence provided by the spectra reported in Figure 21: the overglaze-blue enamel analyzed on the *Flowers and Bird Inside Jar* bowl (Co/Ni ratio of 1.2) proves a perfect match with the blue color detected on the *Phoenix* bowl (Co/Ni ratio of 1.16) fired in the Early Period (1648–1650). The implication is clear: along with the continuity in the use of the Cu-Zn-As-based green, potters in Kaga relied on European *Smalt* for any blue decoration on Ko-Kutani porcelains, from their first inception in the Early Period onward.

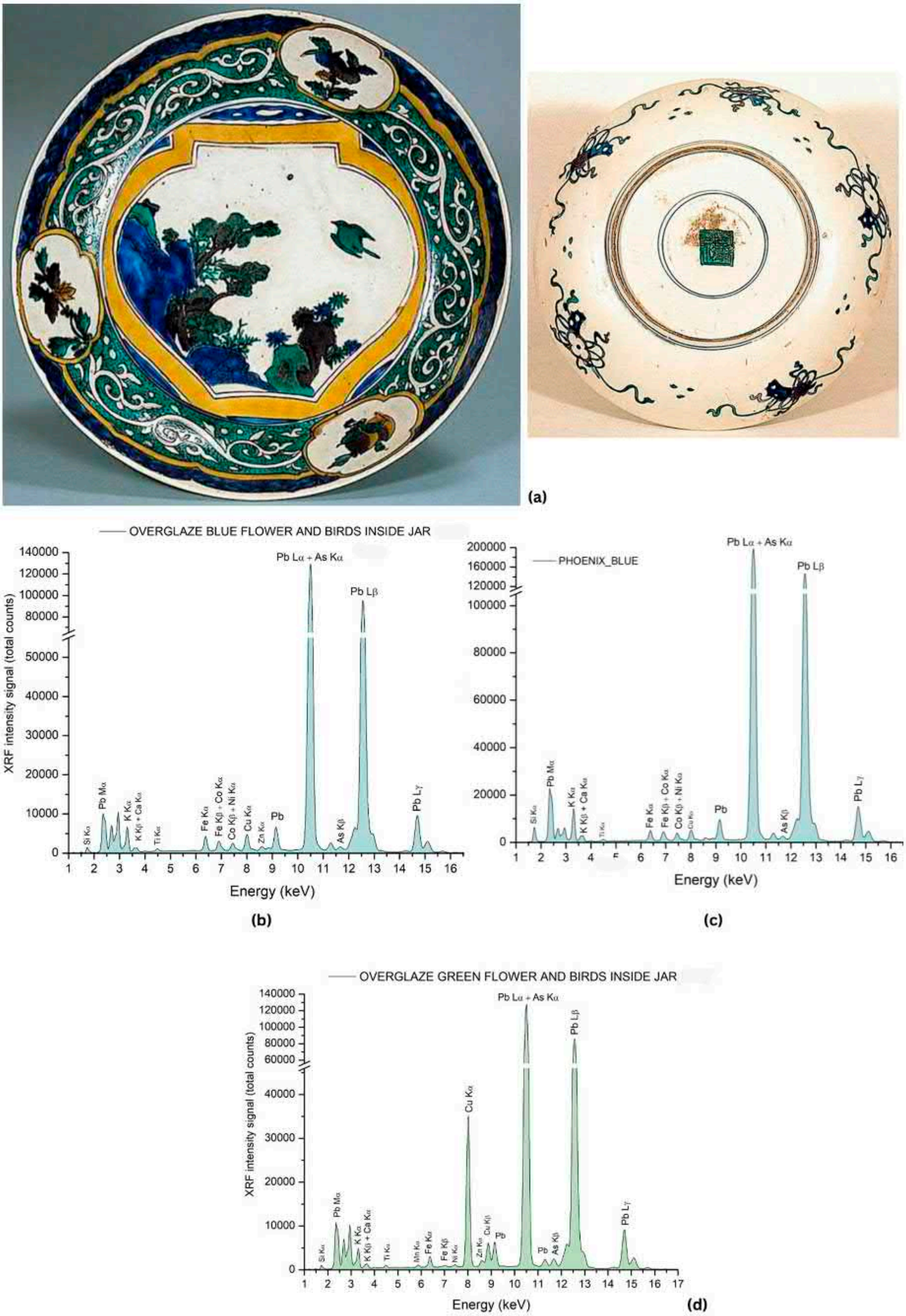


Figure 21. Shallow bowl with design of *Flowers and Bird Inside Jar*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As

chemical composition with high K content) analyzed on the *Flowers and Bird Inside Jar* bowl; (**c**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Phoenix* bowl; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) detected on the *Flowers and Bird Inside Jar* bowl.

Shallow Bowl with Design of *Stream and Mandarin Duck* (1650–1651)

Notable Matches: Blue and Green Enamels

Striking matches are provided by the XRF spectra reported in Figures 22 and 23: the overglaze-blue enamel analyzed on the *Stream and Mandarin Duck* (Co/Ni ratio of 1.17) proves perfectly in line with the blue enamels detected on both the *Flower and Bird Inside Jar* (Co/Ni ratio of 1.2) (Middle Period) and *Phoenix* bowls (Co/Ni ratio of 1.16) (Early Period). As also discussed in Section 3.1.1, the blue material sourced from the deposits in Marienberg (Erzgebirge region, Saxony) proves perfectly consistent with the blue analyzed on the *Phoenix* bowl (Early Period). Moreover, the Cu-Zn-As detected on the *Stream and Mandarin Duck* bowl (Cu/Zn ratio of 26.48) forms an exact pair with the green enamel analyzed on the *Hotei* bowl (Cu/Zn ratio of 27.12) (Early Period). The implication is clear: the European *Smalt*-based blue and the Cu-Zn-As-based green prove to be the foundation of Ko-Kutani enameling throughout the Early and Middle periods.

(a)

Figure 22. *Cont.*

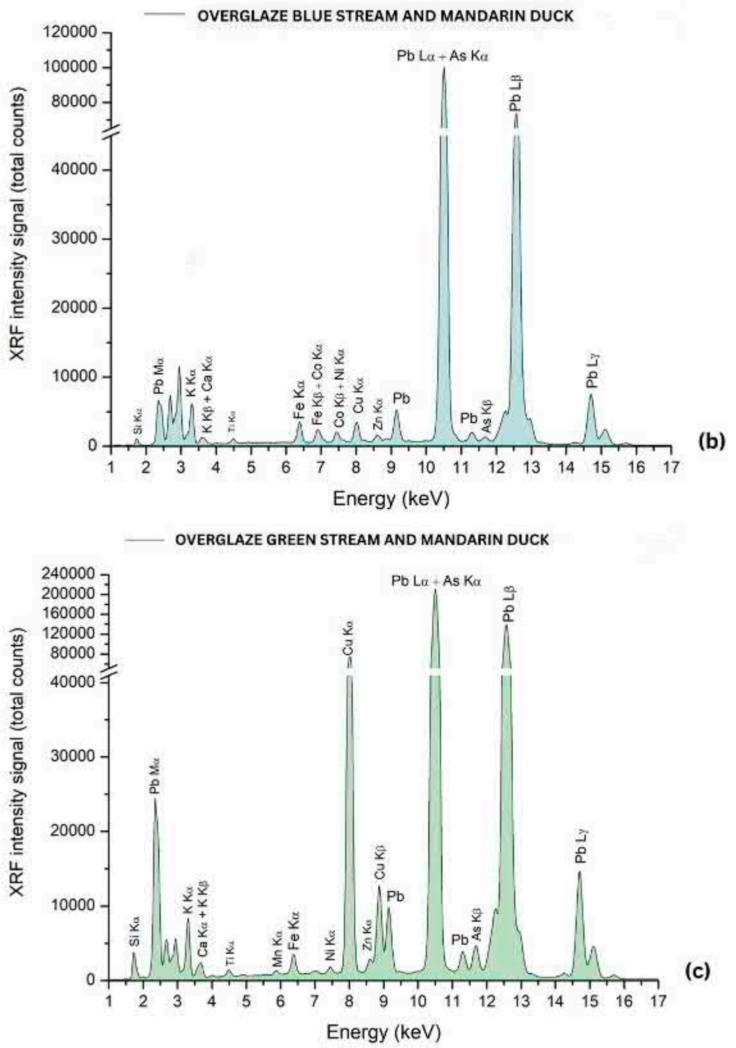


Figure 22. Shallow bowl with design of *Stream and Mandarin Duck*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition).

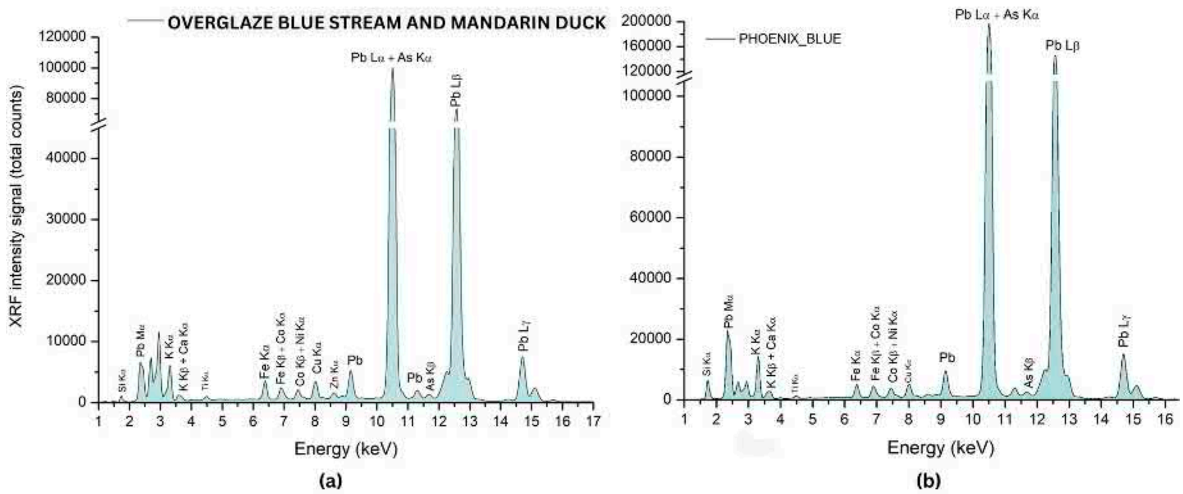


Figure 23. *Cont.*

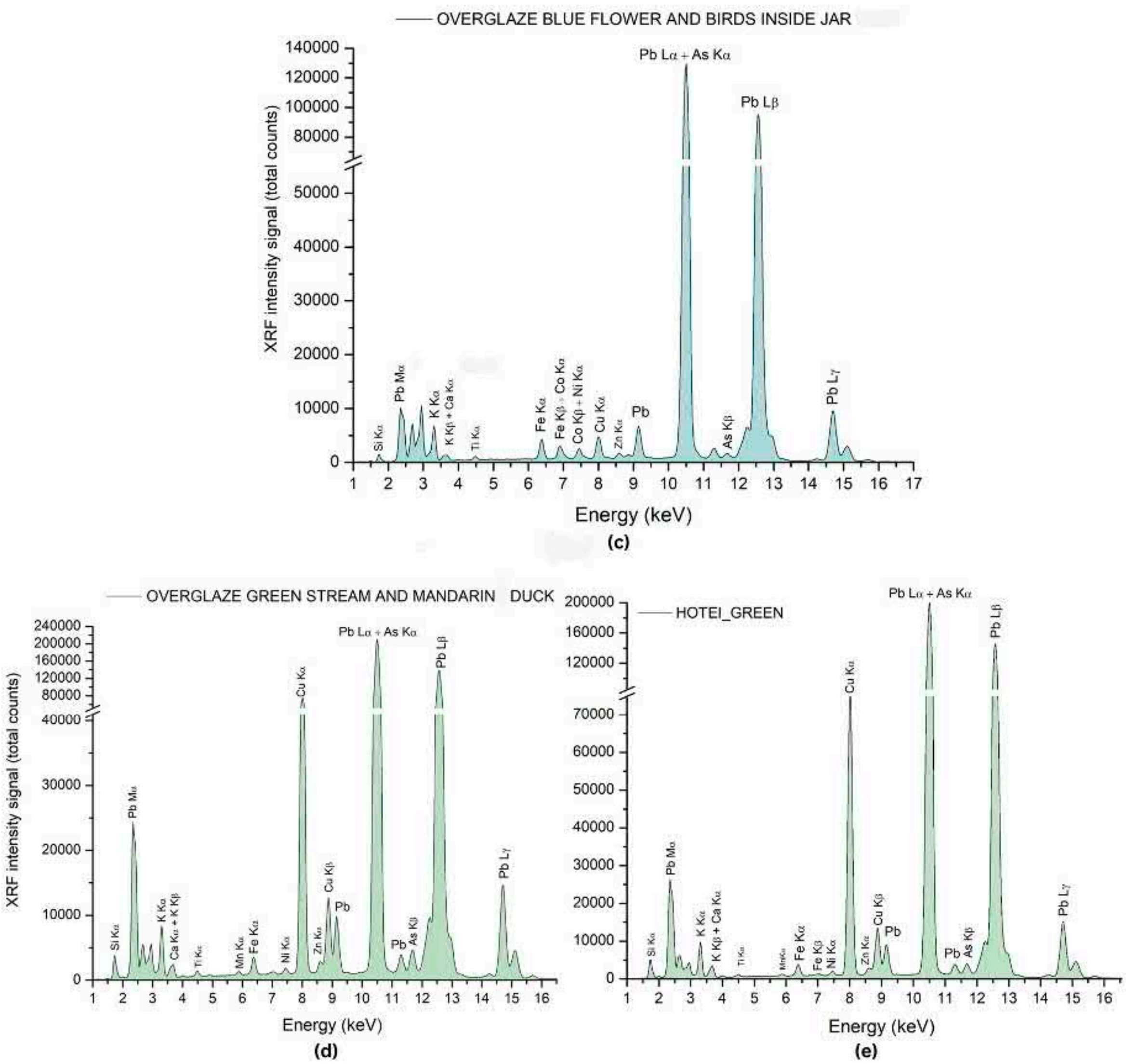


Figure 23. (**a**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the bowl with the *Stream and Mandarin Duck* design; (**b**) XRF spectrum of the overglaze-blue enamel analyzed on the *Phoenix* bowl (1648–1650); (**c**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) detected on the bowl with *Flowers and Bird Inside Jar* design; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Stream and Mandarin Duck* bowl; (**e**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) detected on the *Hotei* bowl (1648–1650).

Shallow Bowl with Design of *Scattered Flowers and Twin Birds* (1650–1651)

Notable Matches—Blue and Green Enamels—Extended

An important instance of the systematic use of *Smalt* for overglaze-blue enameling on Ko-Kutani wares in Kaga comes from the comparison of the spectra reported in Figures 24 and 25: the blue enamel analyzed on the *Scattered Flowers and Twin Birds* bowl (Co/Ni ratio of 1.15) proves a perfect match with the overglaze-blue enamels detected on the *Phoenix* (Co/Ni ratio of 1.16) (Early Period), *Flowers and Bird Inside Jar* (Co/Ni ratio of 1.2) (Middle Period) and *Stream and Mandarin Duck* (Co/Ni ratio of 1.17) (Middle Period) bowls. Such firm consistency emphasizes the strong influence exerted by European Early Period materials on the Middle Period, as further revealed by the match between the green enamels analyzed on the *Scattered Flowers and Twin Birds* (Cu/Zn ratio of 22.12) and *Quail* (Cu/Zn ratio of 22.9) bowls (Figure 25).

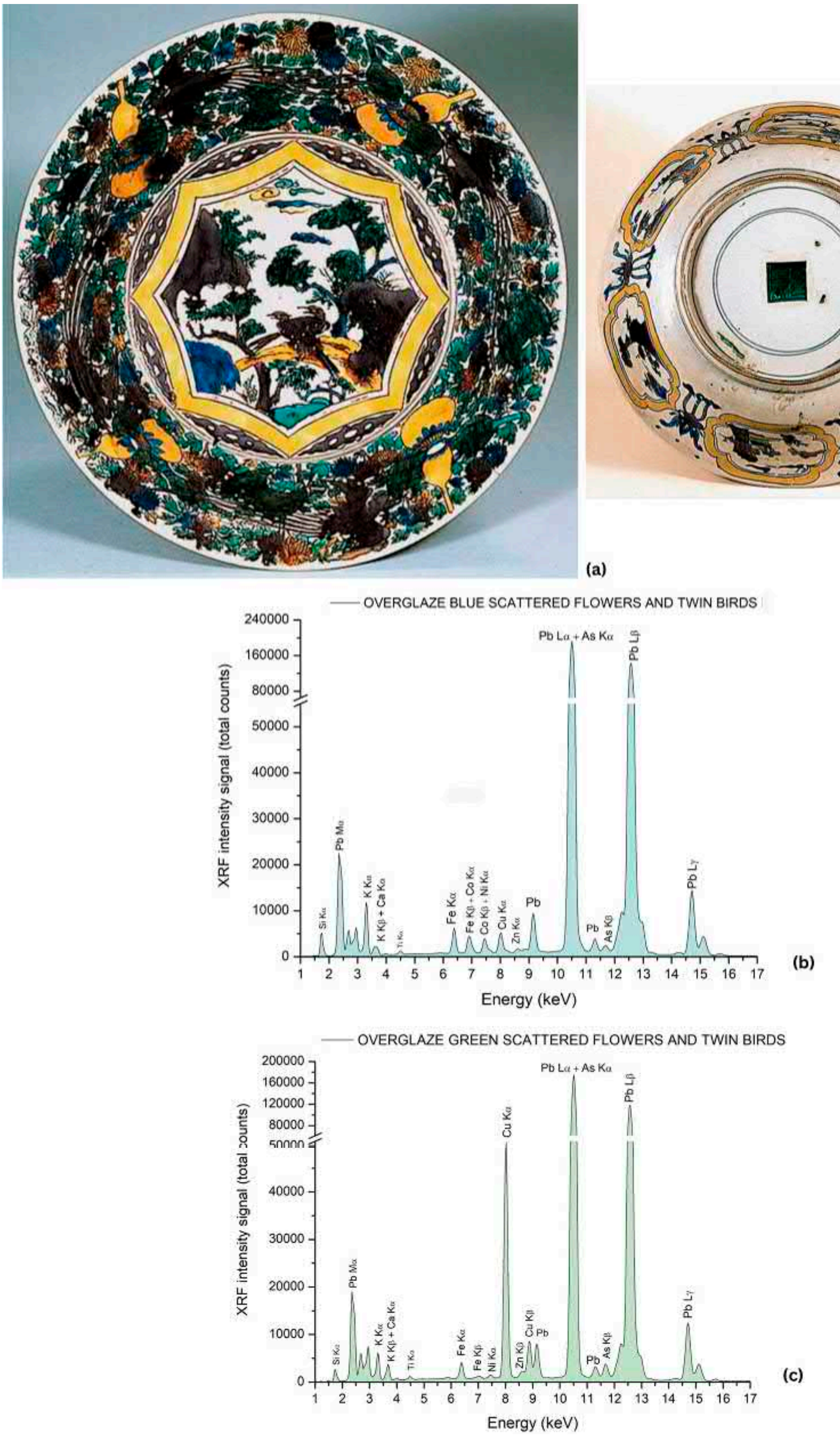


Figure 24. Shallow bowl with design of *Scattered Flowers and Twin Birds*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition).

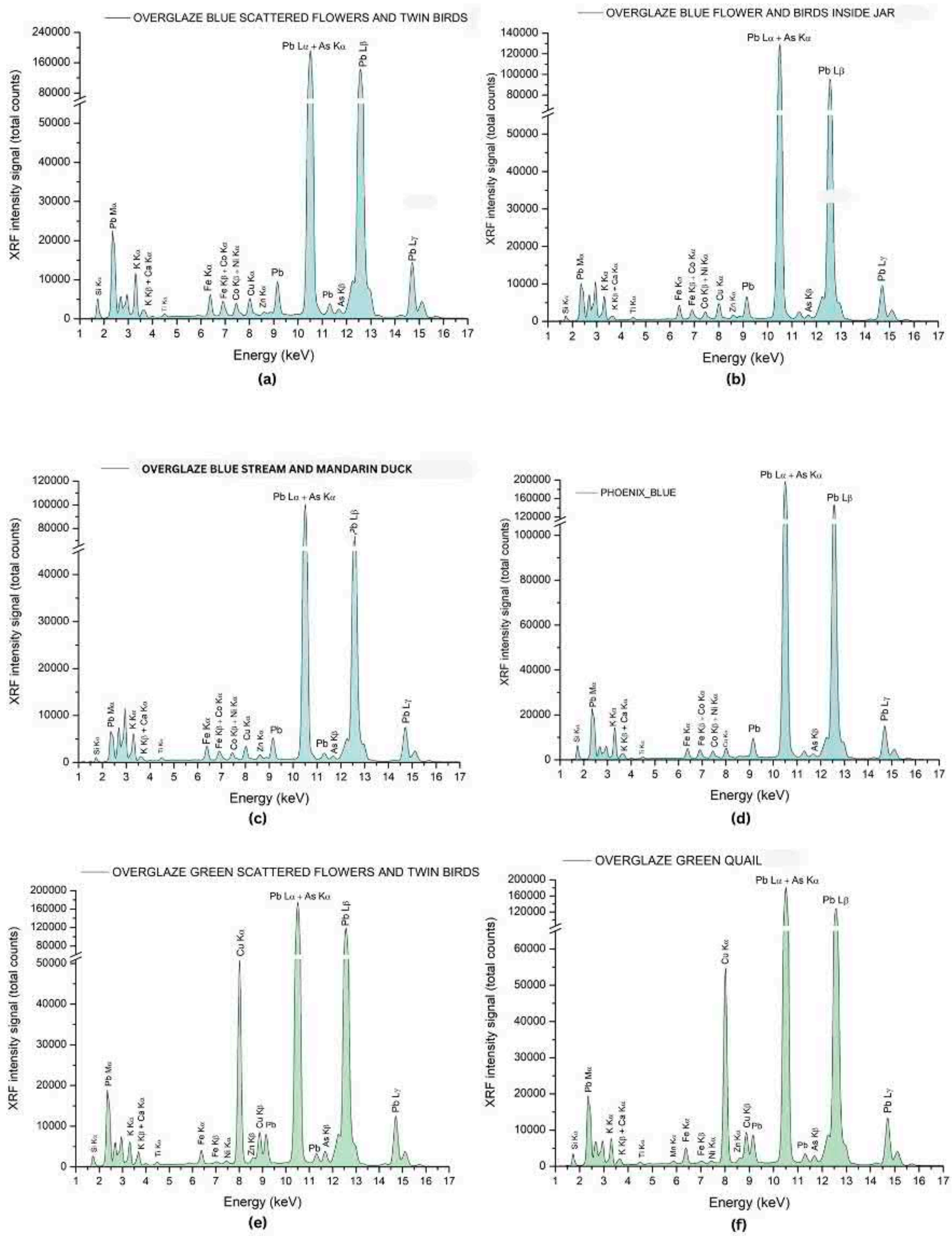


Figure 25. (**a**) XRF spectrum of the overglaze-blue enamels (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Scattered Flowers and Twin Birds* bowl; (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) detected on the *Flowers and Bird Inside Jar* bowl; (**c**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Stream and Mandarin Duck* bowl; (**d**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Phoenix* bowl; (**e**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Scattered Flowers and Twin Birds* bowl; (**f**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) detected on the *Quail* bowl.

Shallow Bowl with Design of *Karuta and Cranes* (1650–1651)

Notable Matches: Green and Enamel

First-time-ever evidence of the systematic use of the Cu-Zn-As chromophore in Kaga comes from the spectra of the green enamels analyzed on the *Karuta and Cranes* (Cu/Zn ratio of 22.9), *Quail* (Cu/Zn ratio of 22.9) and *Scattered Flowers and Twin Birds* (Cu/Zn ratio of 22.12) bowls (Figure 26). The firm consistency provided by such matches, as in the above-mentioned case of *Smalt* for the *Scattered Flowers and Twin Birds* bowl, confirms the crucial role these materials played in establishing the iconic Ko-Kutani styles from their first inception.

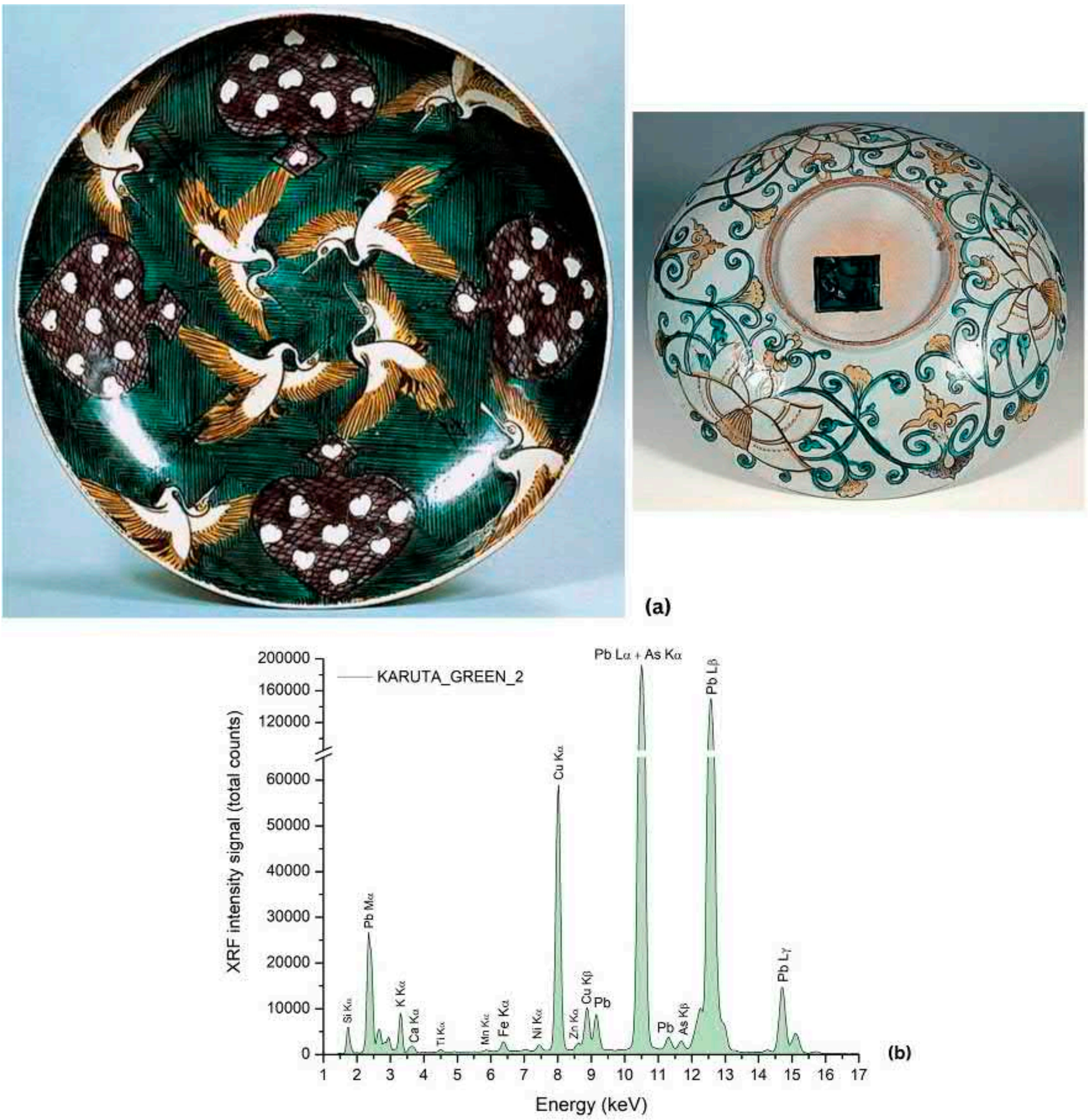


Figure 26. *Cont.*

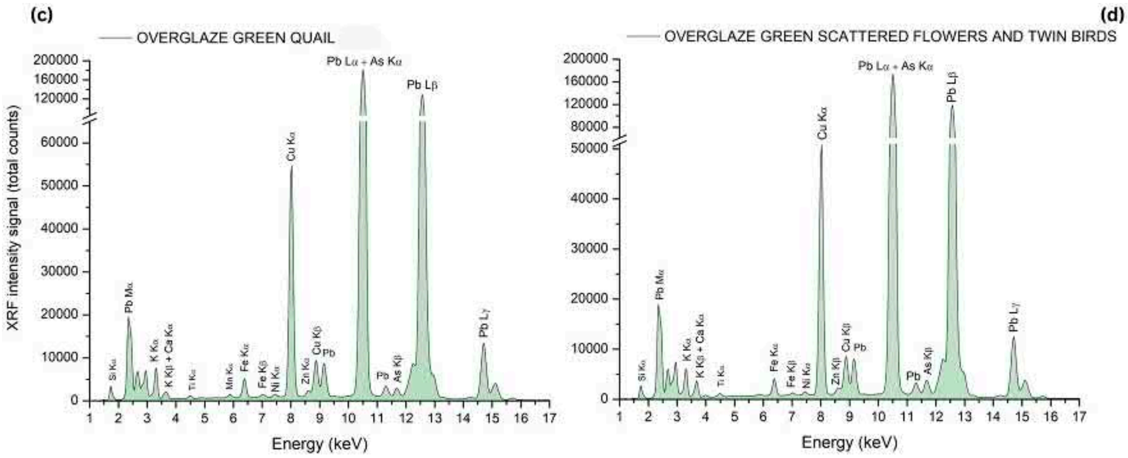


Figure 26. Shallow bowl with *Karuta and Cranes* design: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Quail* bowl; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) detected on the *Scattered Flowers and Twin Birds* bowl.

Shallow Bowl with Design of *Old Tree and White Cloud* (1650–1651)

Notable Features: Decoration Style

The *Old Tree and White Cloud* bowl features an almost completely enameled front, a green-washed underside with black decoration and an unwashed foot (Figure 27). Such transitional characteristics testify to the impending shift from the Proto-Aode to the Full Aode style (Section 3.3).

Figure 27. *Cont.*

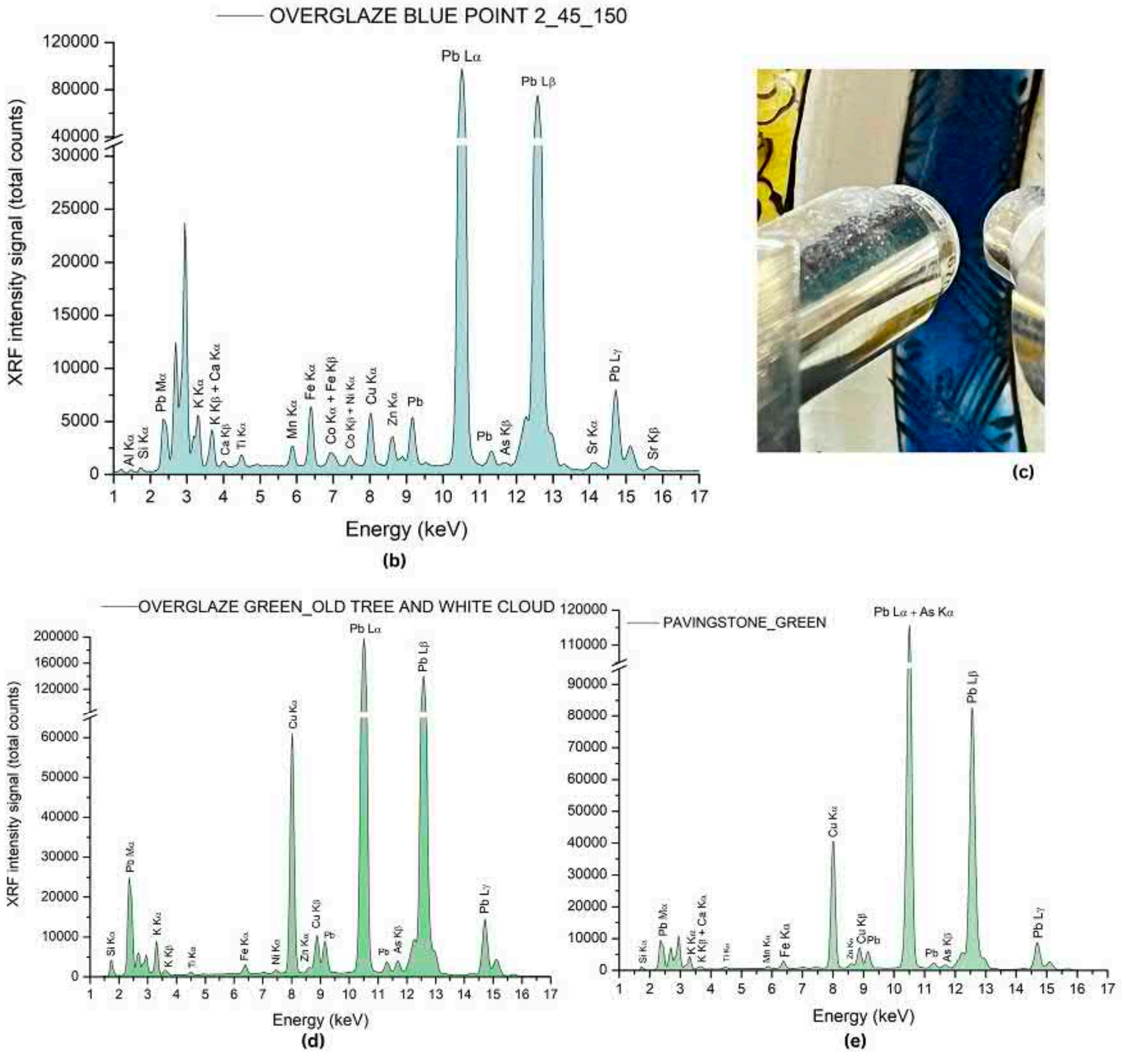


Figure 27. Shallow bowl with design of *Old Tree and White Cloud*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content—the higher Mn and Fe counts are due to the overlapping overglaze-black decoration); (**c**) detail of the blue enamel with overlapping black decoration; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**e**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Paving Stone* bowl.

Notable Matches: Green Enamel

The matching XRF spectra of the green enamels analyzed on the *Old Tree and White Cloud* (Cu/Zn ratio of 18.92) and *Paving Stone Pattern* (Cu/Zn ratio 19.5) bowls (Figure 27) provide first-time-ever evidence of the role the Cu-Zn-As chromophore played during the final transition from the Middle Period to the Late Period (Section 3.3).

3.3. The Late Period (1651–1655)

3.3.1. KO-KUTANI MASTERPIECES—The Late Period and the Full Aode Style (1651–1655)

In the Late Period, the Proto-Aode style reaches its final form and becomes the Full Aode style. The Full Aode style is based on the novel practice of entirely covering the porcelain body with enamels. Blank space is no longer part of the decoration scheme, and it completely disappears also from the underside of the wares. Although strongly innovative, this style change shows a basically conservative approach from a technological standpoint:

XRF results have revealed that potters, consistent with the previous periods, kept relying on European *Smalt* for overglaze blue and on the Cu-Zn-As-based enamel for overglaze green. However, from 1652, the Cu-Zn-As coloring agent would be replaced by the Cu-Zn-based chromophore, the same Ninsei had been employing for overglaze decoration since the establishment of his kiln in Kyoto in 1648 (Section 3.1.2). Analytical evidence, therefore, provides a first-time-ever insight into the practices dominating the last stage of Ko-Kutani production: cost-cutting had become paramount, possibly as a consequence of the increasingly problematic supply of pigments from Europe due to the persecutions, as also confirmed by the overall reduced use of overglaze blue in the palette of choice.

Early Motifs and Materials

The Ko-Kutani porcelains belonging to the Late Period, as in the case of the Middle Period, are listed in the order of their firing, from earliest to latest. The decoration schemes and materials utilized throughout the period are clearly identified and dated. Spectra of the overglaze-blue and overglaze-green enamels are reported. The yellow color will be discussed in Section 3.6.3.

Shallow Bowl with Design of *Shochikubai* (1651)

Notable Features: Decoration style and green enamel

The *Shochikubai* bowl bears stylistic features and materials belonging to both the Middle and Late periods: the front is now completely covered with polychrome enamels, the underside colored with a green wash, and the foot unwashed (Figure 28). Such transitional characteristics testify to the now established Full Aode style, yet in its very initial form (1651). Also proving to be particularly relevant is the presence of the Cu-Zn-As-based green enamel.

Figure 28. *Cont.*

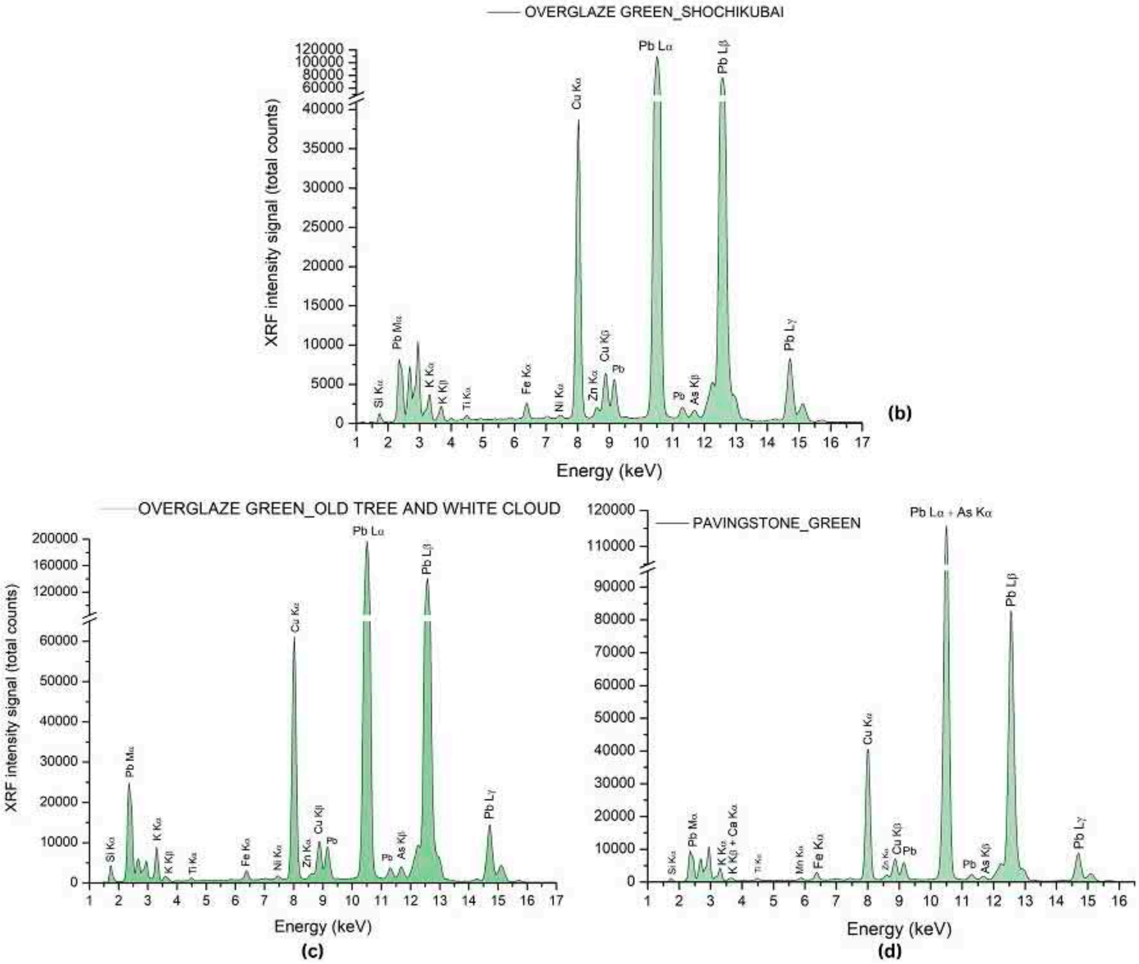


Figure 28. Shallow bowl with design of *Shochikubai*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Old Tree and White Cloud* bowl; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Paving Stone Pattern* bowl.

Notable Matches: Green Enamel

The groundbreaking match provided by the XRF spectra of the green enamels analyzed on the *Shochikubai* (Cu/Zn ratio of 18.73), *Old Tree and White Cloud* (Cu/Zn ratio of 18.92) (Middle Period) and *Paving Stone Pattern* (Cu/Zn ratio of 19.5) (Middle Period) bowls (Figure 28) reveals, for the first time ever, that the inception and early firing of the Full Aode style was based on the very same materials upon which the Proto-Aode style had been developed in the Middle Period.

Such early continuity is firmly confirmed by the basically identical Cu-Zn-As green enamels detected on the *Shochikubai* (Late Period) and *Old Tree and White Cloud* (Middle Period) bowls, with Cu/Zn ratios of 18.73 and 18.92 respectively.

Shallow Bowl with Design of *Peony* (1651–1652)

Notable Features: Decoration Style and Green Enamel

The *Peony* bowl features a completely enameled front. The underside and foot are now entirely covered with a green wash. Moreover, the iconic fluffy snowflakes pattern makes its appearance on both the yellow ground on the front and the green wash on the underside (Figure 29). Also relevant is the consistent use of the Cu-Zn-As-based coloring agent for all green enameling (Figure 29), while yet showing a glossier and more opaque shade.

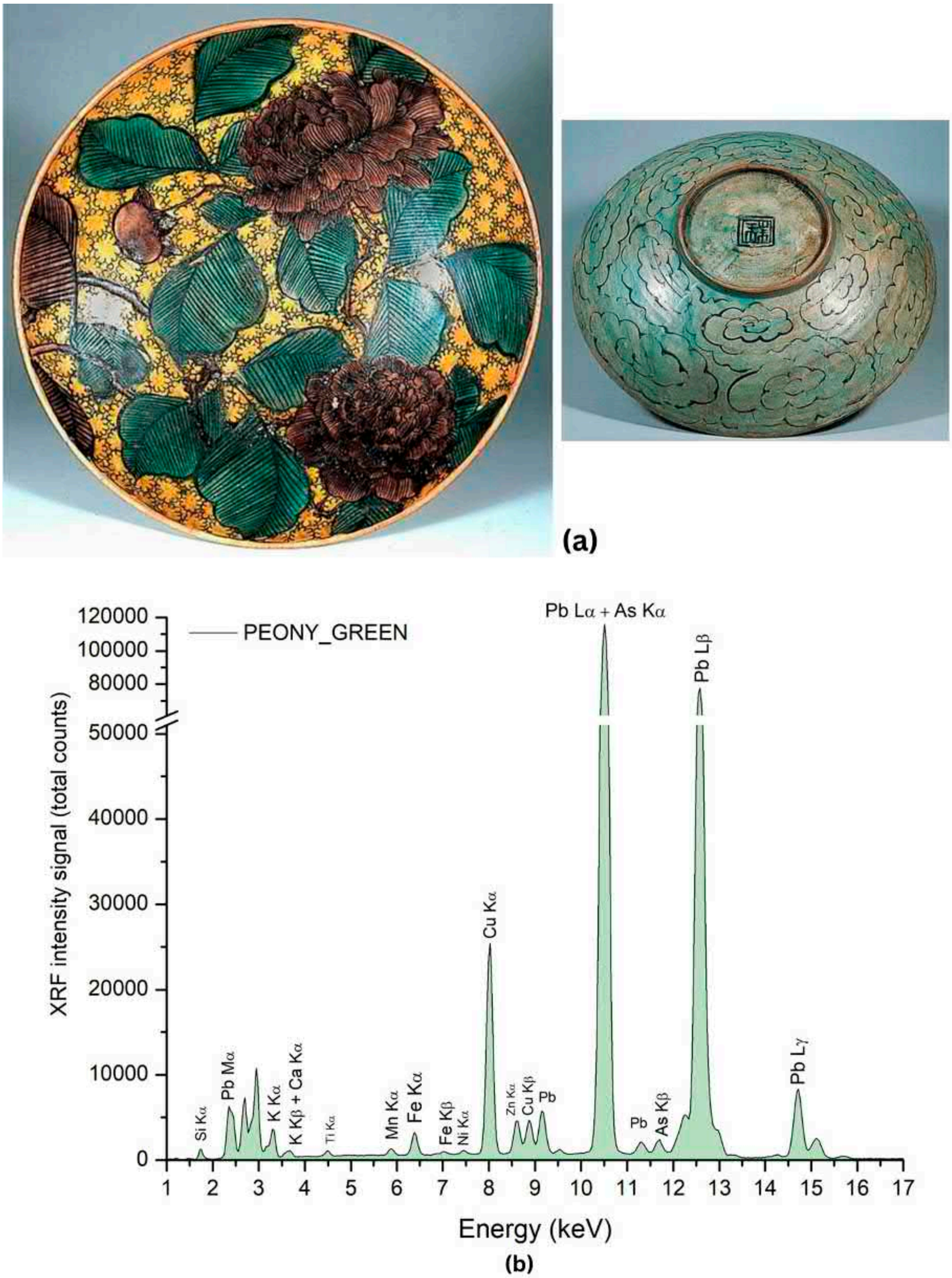


Figure 29. Shallow bowl with design of *Peony* (AODE PEONY): (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition).

Shallow Bowl with Design of Aged Pine Tree (1651–1652)

Notable Features and Matches—Combined—Decoration Style and Green Enamel

The relevant match between the XRF spectra of the green colors reported in Figure 30, unveils, for the first time ever, a transitional stage within the Late Period. The shallow bowls depicted in Figures 28–30 all bear the Cu-Zn-As-based green enamel. As already pointed out for the previous periods, the presence of such a coloring agent enables the identification of the motifs used on the earliest wares. In this particular case, the material is associated with two distinctive decoration patterns: a yellow ground adorned with flower and snowflake outlines on the front, and larger fluffy snowflakes on the green-washed underside. From a technlogical standpoint, a recurring dynamic can be clearly identified on the basis of the analytical evidence presented in this study: potters fired the Cu-Zn-As green first, and then proceeded with the incoproration of the *Smalt*-based blue enamel (also discussed in the following section). Such a distinctive process, belonging to all three periods (Sections 3.1.1 and 3.2.1), has been herein unveiled for the first time ever.

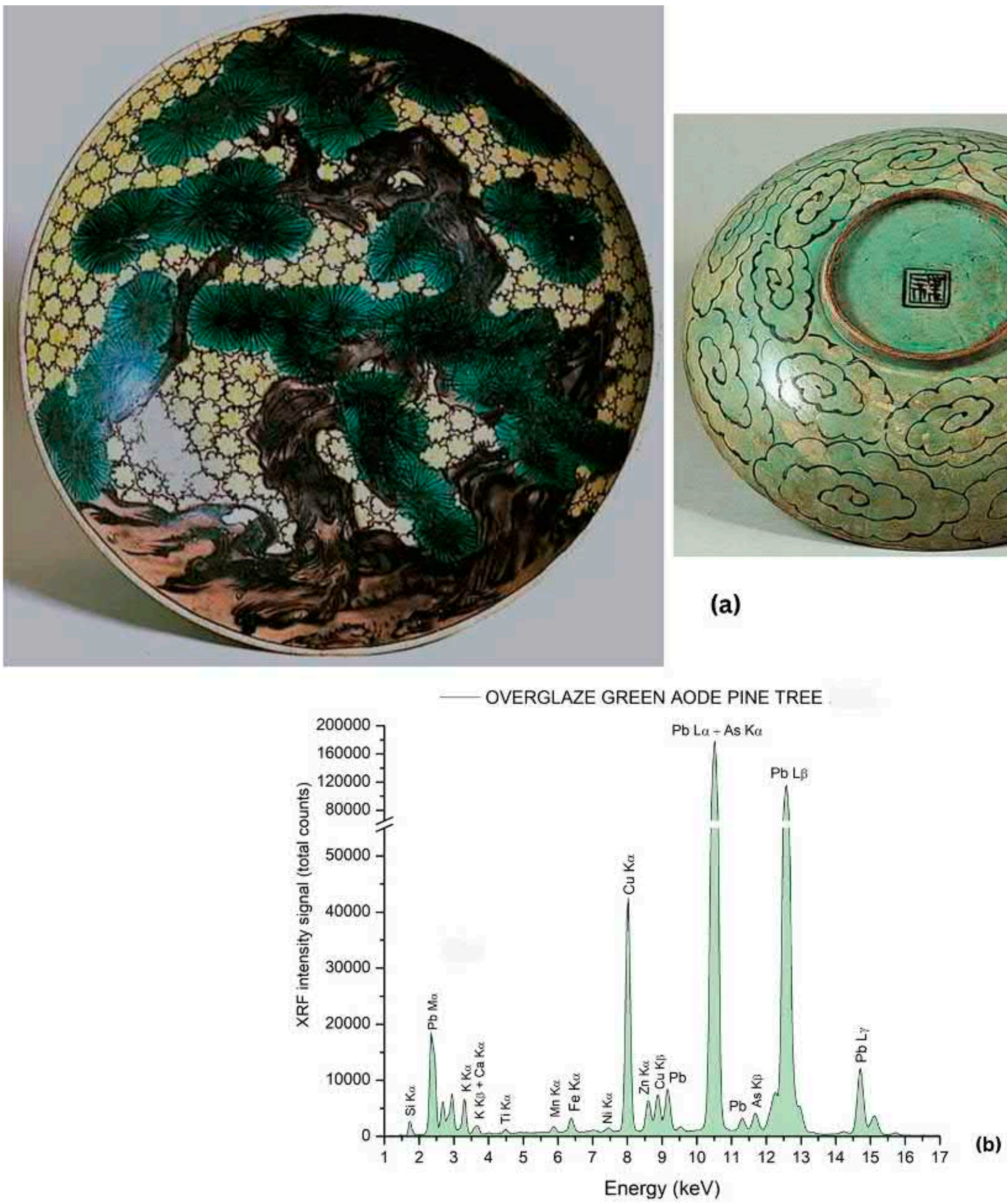


Figure 30. *Cont.*

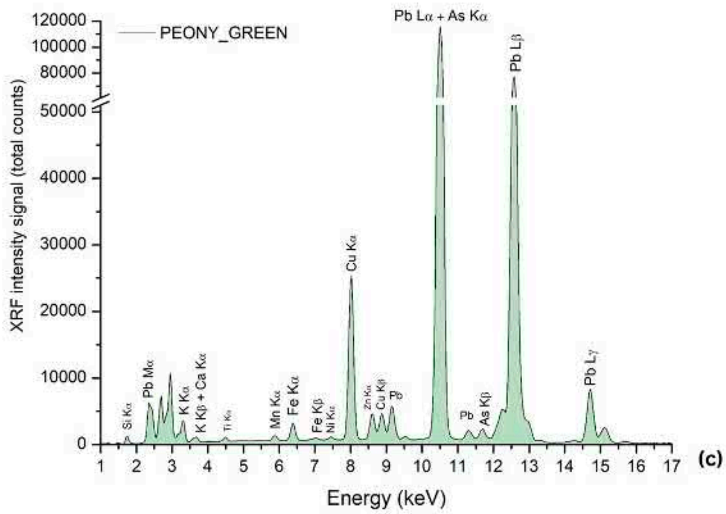


Figure 30. Shallow bowl with design of *Aged Pine Tree* (AODE PINE TREE): (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn-As chemical composition) analyzed on the *Peony* (AODE PEONY) bowl.

Toward the epilogue

A fully matured decoration style would characterize the last phase of Ko-Kutani production in Kaga, right before the kiln was shut down. A description of materials and styles follows.

Shallow Bowl with Design of *Pine Tree and Peacock* (1652)

Notable Features: Decoration style and Green Enamel

The *Pine Tree and Peacock* bowl represents the transition to the final stage of Ko-Kutani production (1652–1655). It bears a very distinctive combination of previous and novel features: the black-outlined flowers on a yellow ground and the fluffy snowflakes still adorn the front and the underside, respectively, while the Cu-Zn-As chromophore is now replaced by the Cu-Zn coloring agent (Figure 31). Moreover, the *Smalt*-based blue enamel is once again used, although on a limited basis, thus revealing how potters in Kaga, after 1652, relied on the very same blue and green enamels Ninsei had incorporated into his wares since their first inception, that is, the Cu-Zn-based green and the *Smalt*-based blue (Section 3.1.2).

Notable Matches: Blue Enamel

An extremely relevant match can be observed between the XRF spectra of the overglaze-blue enamels analyzed on the *Pine Tree and Peacock* (Co/Ni ratio of 1.19) bowl and the *Flowers and Bird Inside Jar* (Co/Ni ratio of 1.2) (Middle Period) bowl (Figure 32): since the European blue color detected on the *Flowers and Bird Inside Jar*, fired in the Middle Period, has also proven a perfect match with the blue enamels utilized in both the Early and Middle periods (discussed in Notable Matches—Blue and green enamels—Extended for the *Scattered Flowers and Twin Birds* bowl), the instance herein presented is a further testament to the strict continuity Kaga potters had based Ko-Kutani firing upon throughout the three periods of production.

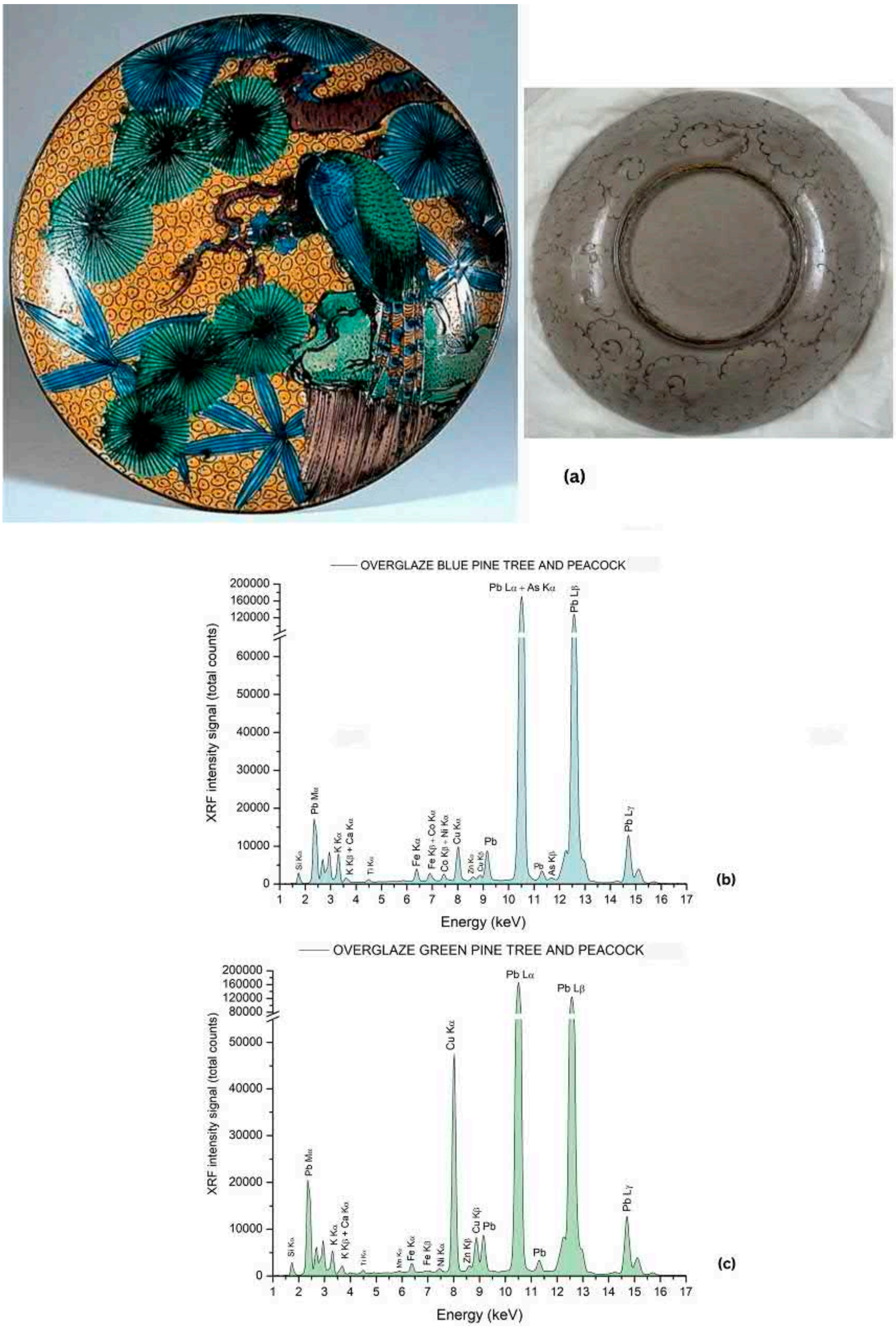


Figure 31. Shallow bowl with design of *Pine Tree and Peacock*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the novel overglaze-green enamel (Cu-Zn chemical composition).

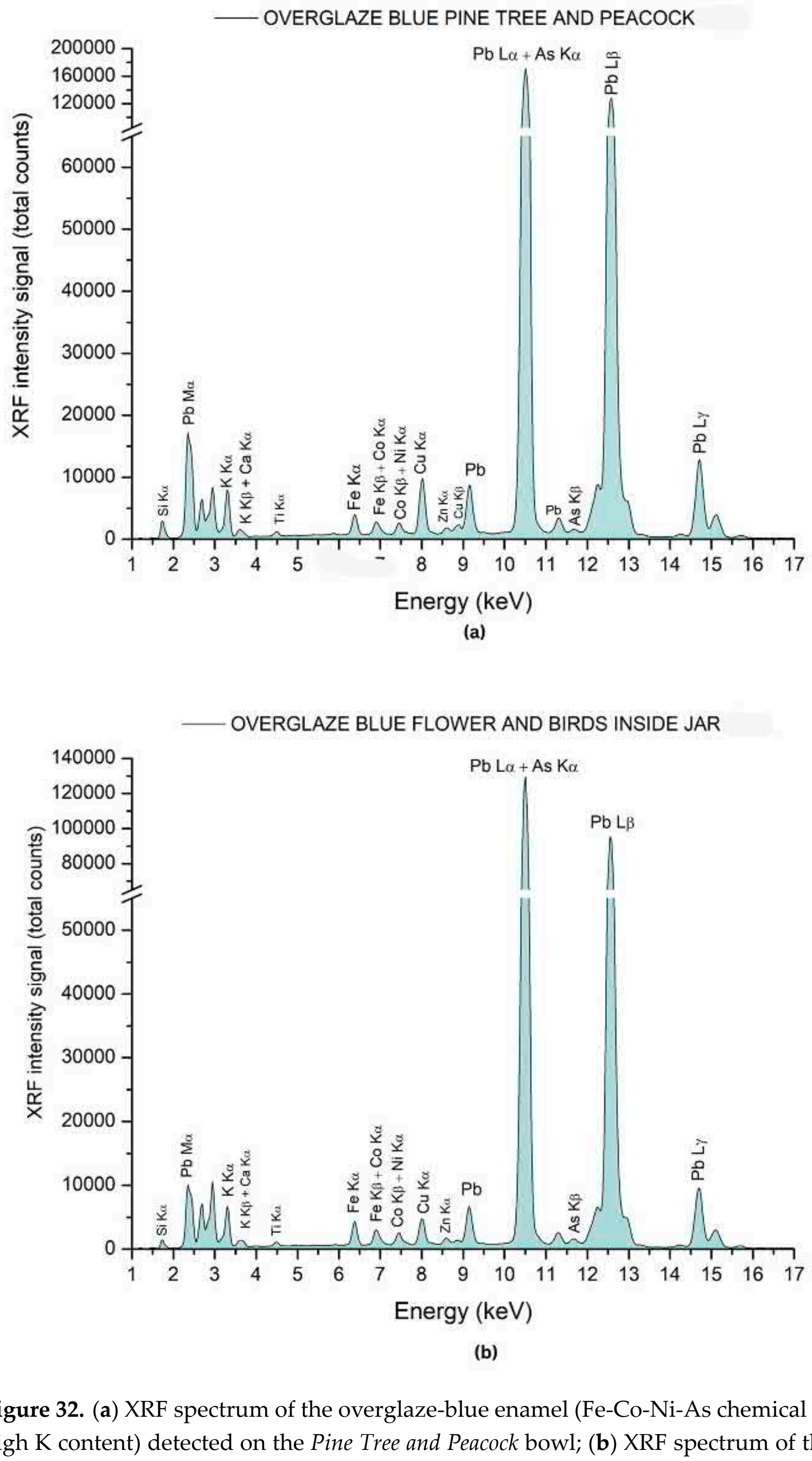


Figure 32. (**a**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) detected on the *Pine Tree and Peacock* bowl; (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Flowers and Bird Inside Jar* bowl.

Shallow Bowl with Design of *Chestnuts and Waves* (1652–1653)

Notable Features: Decoration Style

The black fluffy snowflakes on the underside are now replaced by more intricate floral scrolls (Figure 33).

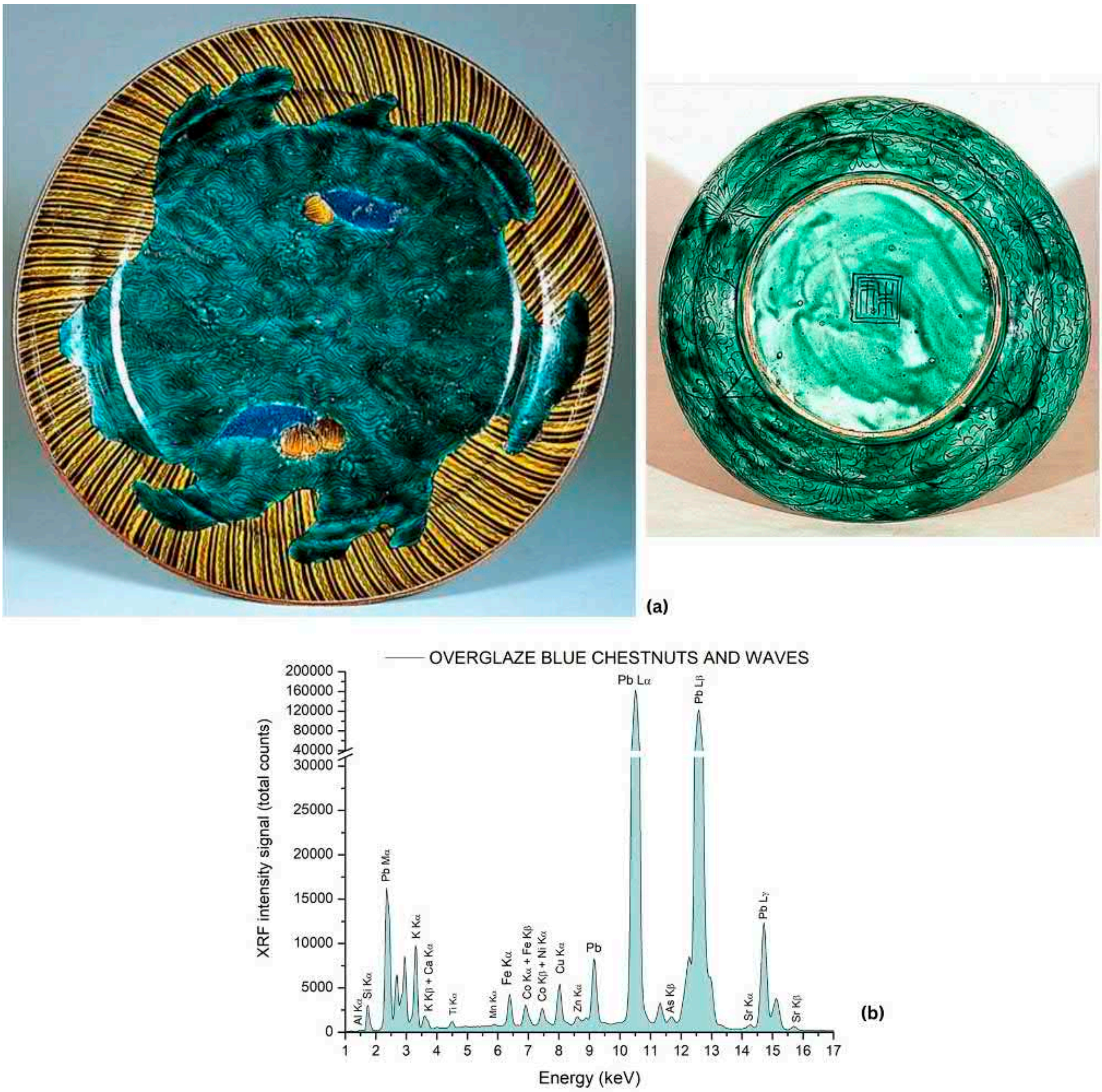
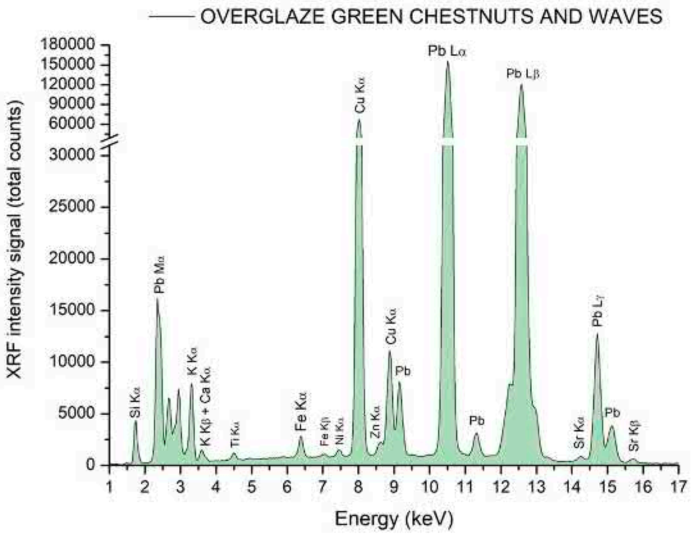


Figure 33. *Cont*.



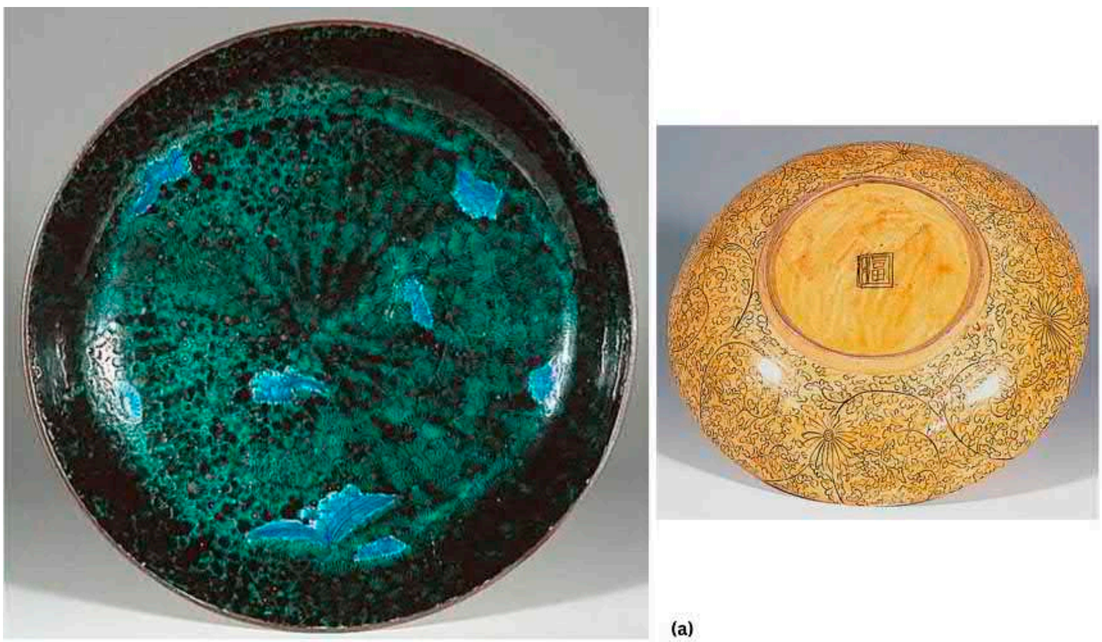
(c)

Figure 33. Shallow bowl with design of *Chestnuts and Waves*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition).

Shallow Bowl with Design of *Scattered Cherry Blossoms* (1653–1654)

Notable Matches: Blue and Green Enamels

Two groundbreaking matches emerge from the XRF spectra reported in Figures 34 and 35. Specifically, the blue enamel analyzed on the *Scattered Cherry Blossoms* (Co/Ni ratio of 1.17) bowl proves perfectly consistent with the blue enamel detected on the *Stream and Mandarin Duck* (Co/Ni ratio of 1.17) fired in the Middle Period. Since the latter has also proven a perfect match with the blue enamels utilized in the Early Period, as previously discussed in Notable Matches—Blue and green enamels—Extended for the bowl with the design of *Scattered Flowers and Twin Birds*, the *Scattered Cherry Blossoms* bowl offers a precious instance of the continuity that marked Ko-Kutani production throughout all three periods and styles.



(a)

Figure 34. *Cont.*

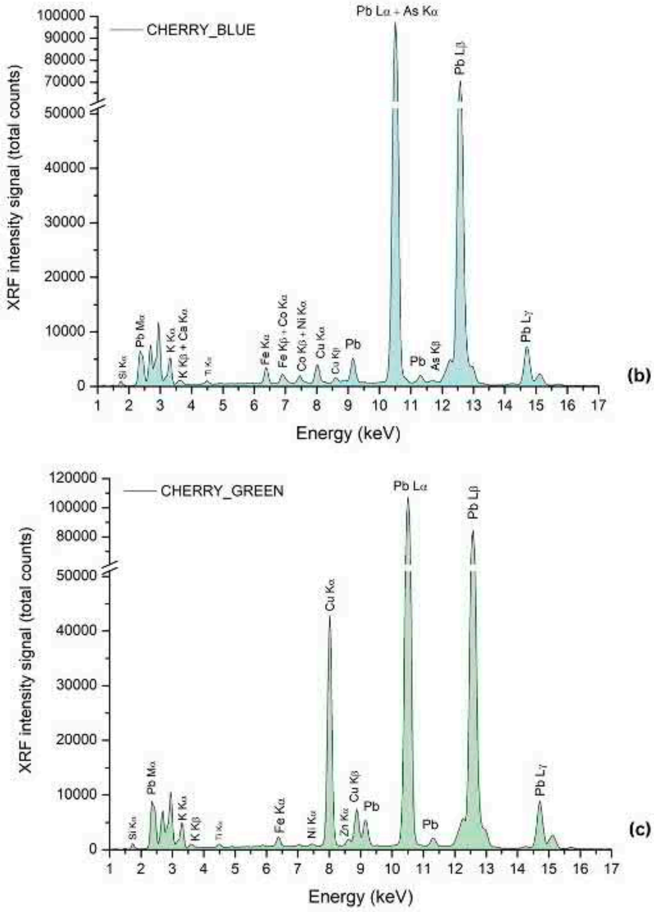


Figure 34. Shallow bowl with design of *Scattered Cherry Blossoms*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content); (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition).

Moreover, the *Scattered Cherry Blossoms* bowl provides further proof of the influence exerted by the Kaga potters on Nonomura Ninsei during his stay in the Maeda fiefdom: the Cu-Zn-based green chromophore analyzed on the *Scattered Cherry Blossoms* bowl (Cu/Zn ratio of 21.9) matches the Cu-Zn-based coloring agent detected on Ninsei's Water Jar (*Mizusashi*) (Cu/Zn ratio of 22.3) (Figure 35). Since the green enamel analyzed on Ninsei's Water Jar (*Mizusashi*) also proves a match with the Italian majolica green (Saint) as discussed in Section 3.1.2, such first-time-ever evidence unveils the common European origin of the materials upon which the inception and firing of both the Ko-Kutani and Ninsei's wares had been based.

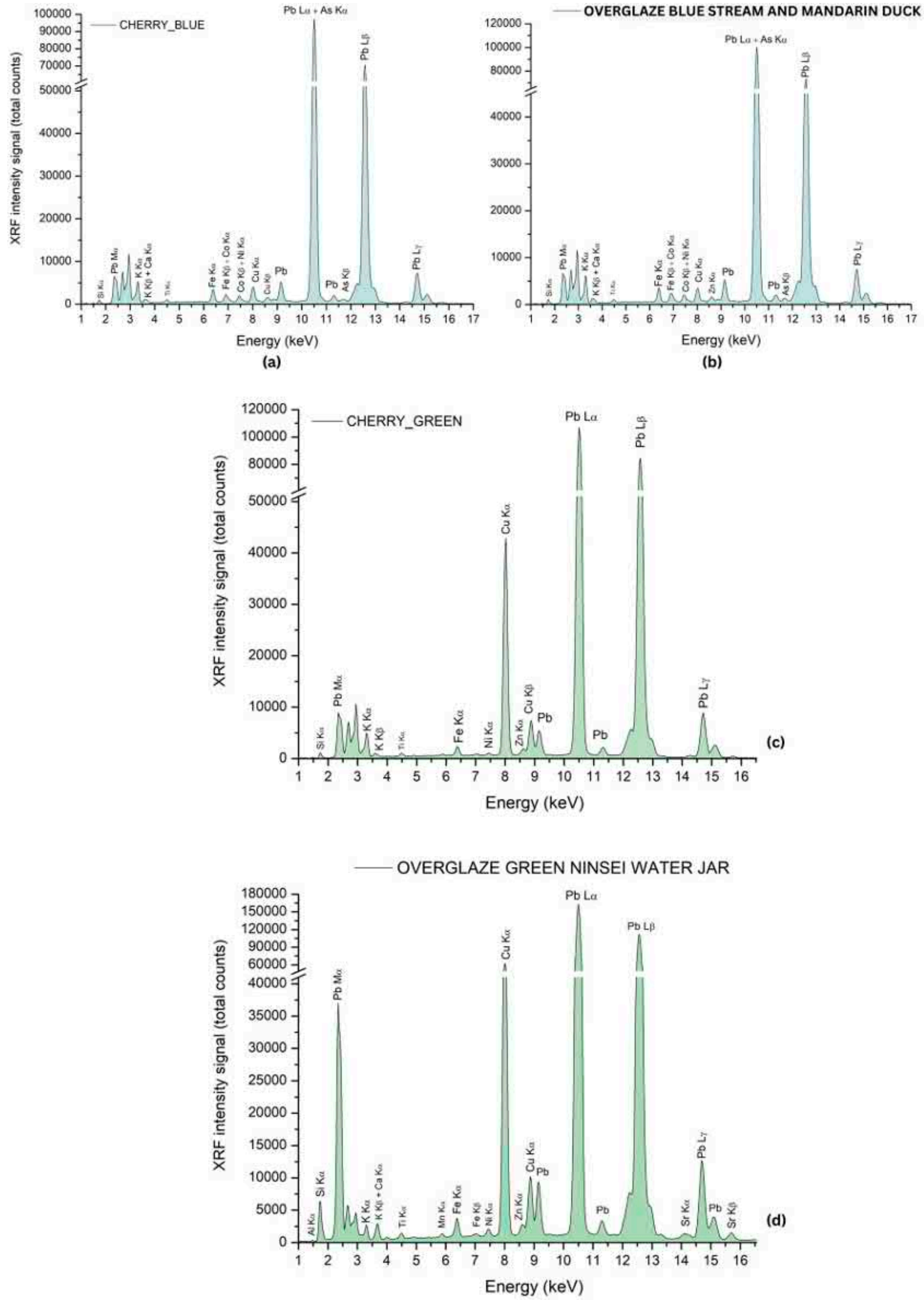


Figure 35. Shallow bowl with design of *Scattered Cherry Blossoms*: (**a**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on the *Scattered Cherry Blossoms* bowl; (**b**) XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) detected on the *Stream and Mandarin Duck* bowl; (**c**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition) analyzed on the *Scattered Cherry Blossoms* bowl; (**d**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition) detected on Ninsei's Water Jar (*Mizusashi*).

Shallow Bowl with Design of *Grapevine* (1653–1654)

Notable Features: Decoration Style and Green Enamel

The grapevine motif featured on the Ko-Kutani bowl clearly mimics the distinctive compostions of European early 17th-century still-life paintings and decorations found on a gilt-and-lacquer *Namban* chest produced in Kyoto for the European market in the early 17th century. As for the materials detected on the bowl, the green enamel proves consistent with the Cu-Zn-based chromophore used throughout the Late Period. The yellow enamel will be discussed in Section 3.6.3.

Shallow Bowl with Design of *Jumokuzu* (*Big Tree*) (1654–1655)

Notable Features: Green Enamel and Decoration Style

The final stage of Ko-Kutani production, as seen in Figures 33, 34, 36 and 37, is charaterized by changes in decoration patterns and enameling material: in particular, the fluffy snowflakes on the underside are abandoned in favor of more intricate floral scrolls, and the Cu-Zn-based green enamel replaces its Cu-Zn-As-based predecessor. Overglaze blue is still incorprated into the overall design, yet in a somewhat restrained fashion and limited to specific motifs. Moreover, the black-outlined flowers and snowflakes on the front of the bowls give way to more complex and symbolic motifs. To conclude, for the first time ever, it is has become possible to differentiate between the initial Full Aode decoration and late Full Aode motifs on the basis of scientifc evidence, thus providing a fundamental tool for a precise dating of the wares.

(a)

Figure 36. *Cont.*

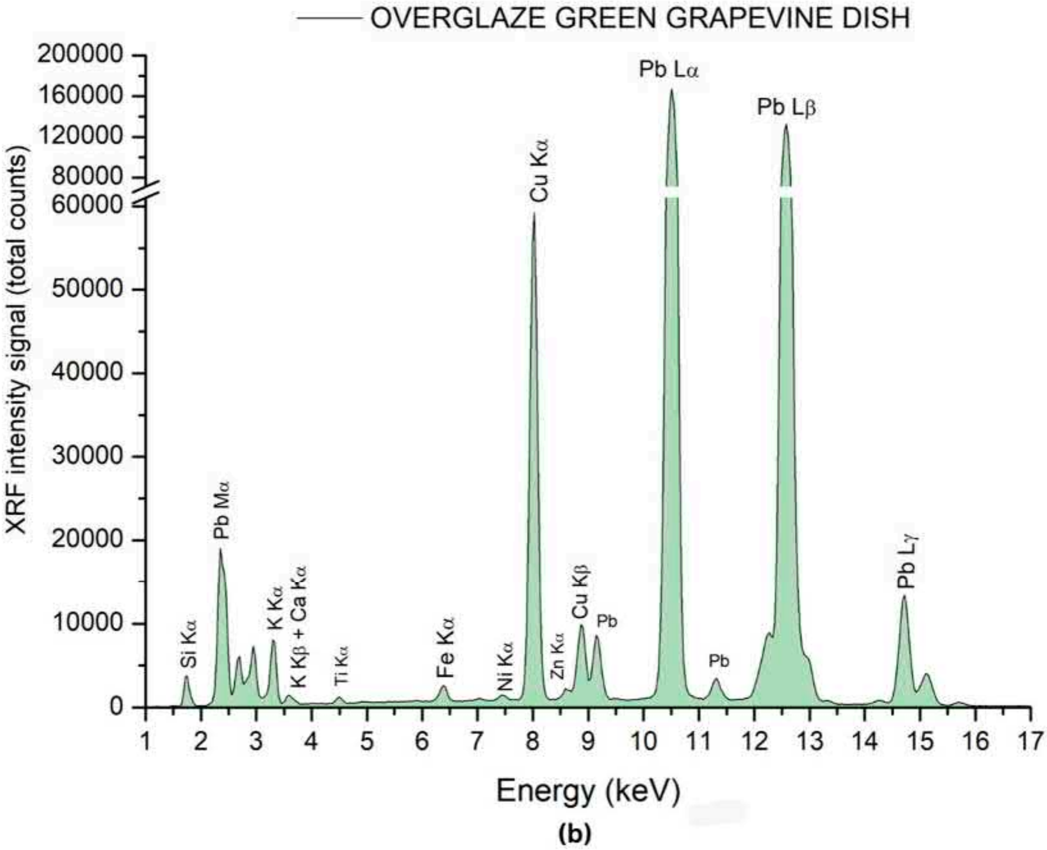


Figure 36. Shallow bowl with design of *Grapevine*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the overglaze-green enamel (Cu-Zn chemical composition) analyzed on the *Grapevine* bowl.

Figure 37. *Cont.*

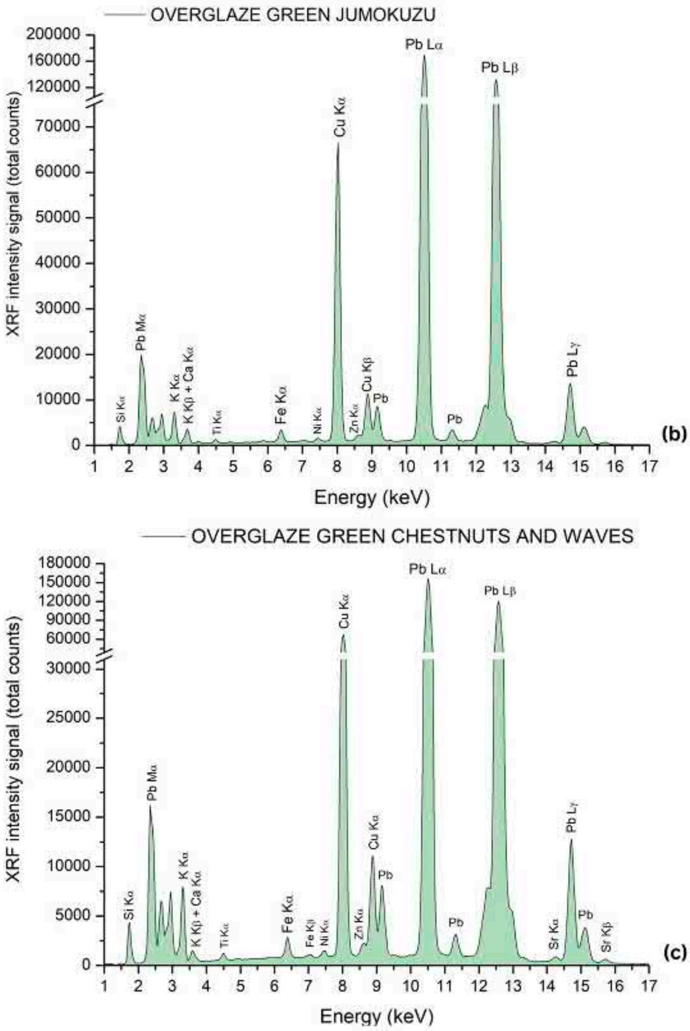


Figure 37. Shallow bowl with design of *Jumokuzu (Big Tree)*: (**a**) Front and underside (Collection of Ishikawa Prefectural Museum of Art); (**b**) XRF spectrum of the green enamel (Cu-Zn chemical composition); (**c**) XRF spectrum of the green enamel (Cu-Zn chemical composition) detected on the *Chestnuts and Waves* bowl.

Notable Matches: Green Enamel

The XRF spectra reported in Figure 37 provide important evidence regarding the consistency of the materials used throughout the Late Period: specifically, the Cu-Zn-based green enamel analyzed on the *Jumokuzu (Big Tree)* (Cu/Zn ratio of 29.93) bowl proves a perfect match with the Cu-Zn-based green enamel detected on the *Chestnuts and Waves* (Cu/Zn ratio of 30.03) bowl (Figure 37). A precise choice of materials, therefore, played a crucial role in the Kaga potters' monumental effort to establish an artistic and cultural legacy that still to this day conveys the strength and depth of the spirit of the Maeda clan.

3.4. Summary of the Results

Overglaze enamels: Co/Ni and Cu/Zn ratios throughout the three periods

The charts in Figures 38 and 39 show the distribution of the Co/Ni and Cu/Zn ratios detected on the Ko-Kutani porcelains for each of the three periods. In order to minimize the effect of the enamel matrix, we have selected the most relevant elements for the two chromophores: cobalt and nickel for the blue, and copper and zinc for the green.

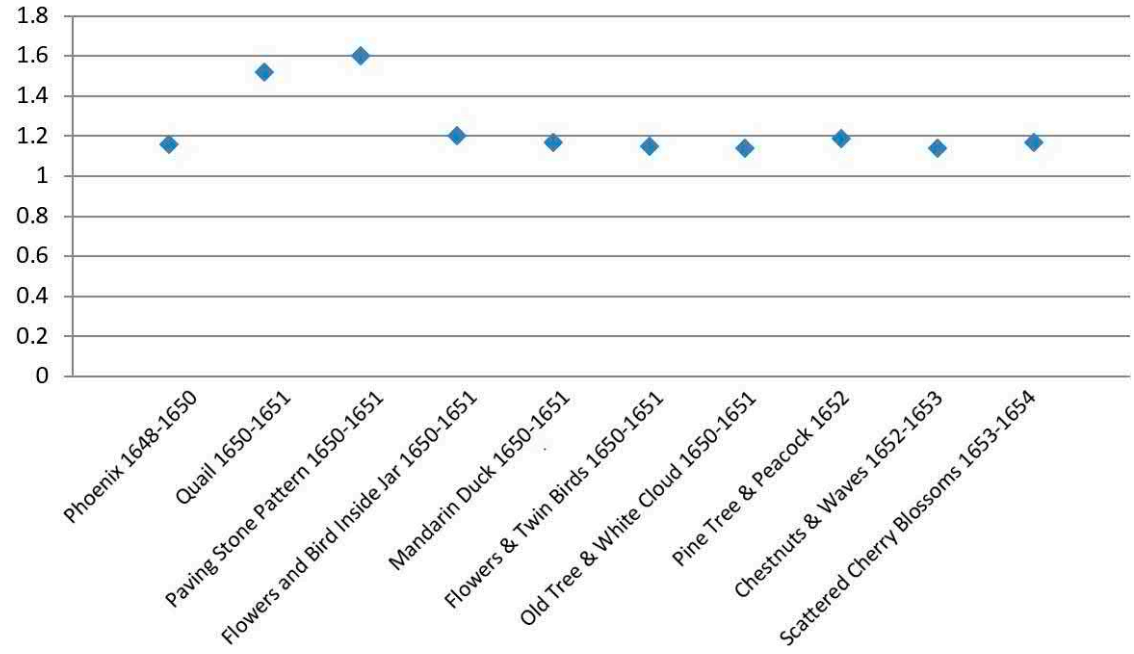


Figure 38. Co/Ni ratios detected on the analyzed Ko-Kutani porcelains in each of the three periods.

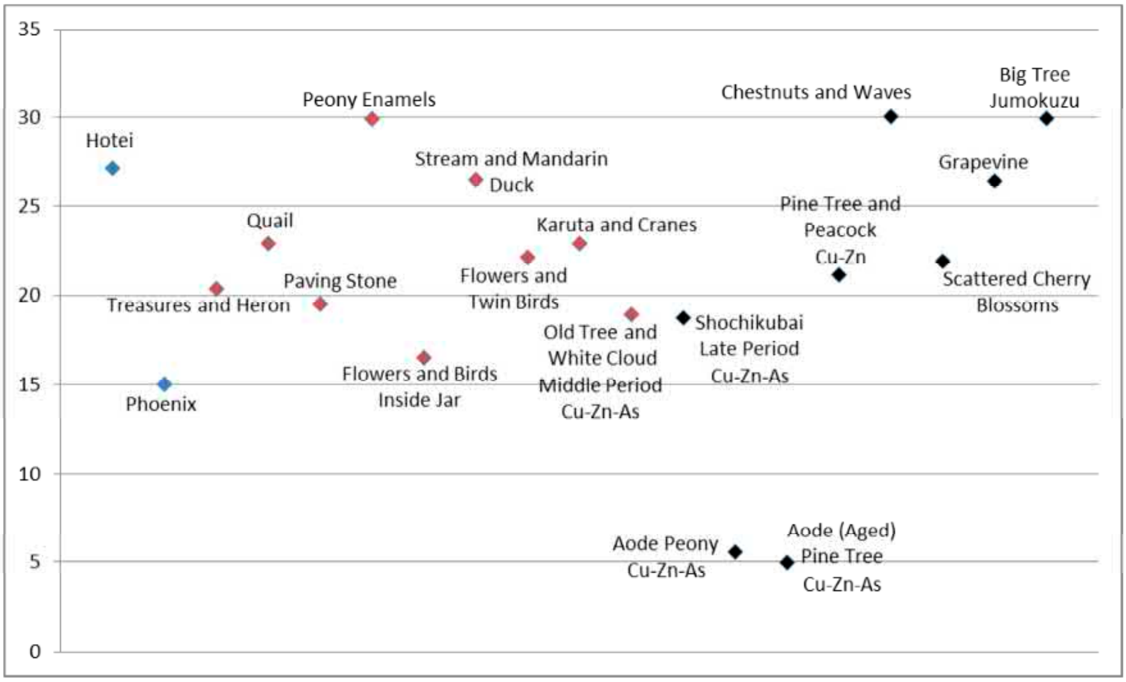


Figure 39. Cu/Zn ratios detected on the analyzed Ko-Kutani porcelains in each of the three periods. From left to right: blue color for the Early Period (1648–1650); red color for the Middle Period (1650–1651); black color for the Late Period (1651–1655).

3.4.1. Blue Enamel: Co/Ni Ratio

The analyzed Ko-Kutani porcelains are represented in three different colors based on the order of their firing (earliest to latest) (Figure 38): from left to right, dark blue for the Early Period, light blue for the Middle Period and turquoise for the Late Period. The Co/Ni ratios distribute evenly around the range of values 1.14–1.2. The only two exceptions belong to the beginning of the Middle Period (1650–1651), with values exceeding the average range shared by all the other Ko-Kutani porcelains. This instance unveils two major dynamics. In order to successfully incorporate *Smalt* into overglaze enameling, potters in Kaga needed to rely on ready-to-use materials imported from Europe. The higher Co/Ni ratios detected on the *Quail* (Co/Ni ratio of 1.52) and *Paving Stone Pattern* (Co/Ni ratio of 1.6) bowls testify to a short-lived experimentation that was almost immediately abandoned. The crucial reason behind such a firm choice is, as previously mentioned, that Japanese potters did not succeed in producing synthetic blue materials and *Smalt*, locally, until the late 19th century, after the ban on Christianity issued in 1614 had finally been lifted in 1873 and the European presence had allowed, under the strong westernization policy enforced by the Emperor Meiji (1868–1912), the establishment of a full-fledged, state-of-the-art industry with the incorporation of preparative chemistry for the production of purified chemical compounds such as carbonates, sulfates, nitrates and oxides [9,22].

3.4.2. Green Enamel: Cu/Zn Ratio

As introduced in the previous section, the analyzed Ko-Kutani porcelains are represented in three different colors based on the order of their firing (earliest to latest) (Figure 39): from left to right, blue for the Early Period, red for the Middle Period and black for the Late Period. The distribution of the Cu/Zn ratios is characterized by an expected variability. Besides the first-time-ever matches identified within the three main groups formed by the wares (discussed throughout the preceding sections), one particular aspect emerges from the chart: a thorough experimentation marked the transition from period to period. This is particularly evident in the case of the Middle-to-Late-Period transition: the *Old Tree and White Cloud* (Cu/Zn ratio of 18.92) and *Shochikubai* (Cu/Zn ratio of 18.73) bowls share both the same Cu-Zn-As chemical composition and Cu/Zn ratio. The apparent continuity in the use of such material, though, is immediately contradicted by the completely different ratios detected on the *Aode Peony* (Cu/Zn ratio of 5.5) and *Aged Pine Tree* (Cu/Zn ratio of 4.96) bowls, grouped at the far bottom and therefore segregating from all the other porcelains. The implication is clear: although the Cu-Zn-As-based green enamel still proves the predominant material upon which the transition is based, the different ratios testify to the experimentation that accompanied the impending shift to the mature Full Aode style, a process that would be completed with the final switch to the Cu-Zn-based chromophore as detected on the *Pine Tree and Peacock* bowl. To conclude, contrary to the case of the standardized employment of ready-to-use *Smalt*-based blue enamel, the green color underwent various modifications to best suit developing styles. Overall, an experimentation–stabilization process can be identified by observing the distribution of the Cu/Zn ratios throughout the three periods.

3.5. Summary of Visual and Design Characteristics

3.5.1. The Inception of the Proto-Aode and Full-Aode Decorations: Western-Style Painting on Porcelain

The results presented so far cast new light, for the first time ever, on the inception of the distinctive Proto-Aode and Full Aode styles. The employment of a uniform and subdued white ground upon which painted motifs would stand out (Section 3.1.1), along with the later development of an entirely enameled body (Section 3.3.1), reveal that color and design were favored over pictorial means, the porcelain body in this case. Such an innovative practice was unquestionably the result of European influence: in the painting tradition of the Old Continent, the canvas is completely covered with overlapping layers of preparation, ground and pigments [33], much like the visual effect of the *Istoriato* wares introduced by Casteldurante (Italy) potters in the early Renaissance period to meet the taste of European noblemen [14] (Figure 40). This last instance further reveals the deep significance of Ko-Kutani decoration and the Maeda's mindset behind it: the creation of a refined yet bold style that would merge the European technological and artistic trends of the 16th and 17th centuries with traditional Japanese aesthetics.

The Proto-Aode and Full Aode styles, therefore, proved an iconic and unparalleled technical achievement that successfully brought together European painting and enamels on porcelain, giving birth to the first-ever-created "Western-Style Painting on Porcelain" in the Far East. The origin of such a groundbreaking innovation can be easily recognized as coming from the already established practice experimented on by Japanese and Chinese painters who had trained at the Jesuit *Seminario* supervised by Father Cola from the late 16th century and testified to by the screens and paintings in a Western style (Figures 10 and 15) that survive in Japan to the present day [33].

Figure 40. (**a**) Majolica dish decorated in *Istoriato* style, Italy, early 17th century (private collection); (**b**) dish decorated with overglaze enamels for the domestic market, Arita ware, 1660s (private collection).

3.5.2. Western-Style Painting on Porcelain: Its Transfer to the Yanbeta Kiln in Arita

The new "Western-Style Painting on Porcelain" that developed in Kaga in the early 1650s unquestionably set apart Ko-Kutani wares from Arita porcelains, the latter being uninterruptedly influenced by Chinese-inspired decoration motifs [48] (Figure 40). From a business-oriented perspective, Ko-Kutani production ceased at Kaga in the latter half of the 1650s, and potters skilled both in Western-style decoration and blue-enameling with *Smalt*, twenty years after their expulsion from Arita due to the first reorganization of the kilns in 1637, faced the need to find new opportunities to survive in the trade once again. Moving back to the now full-fledged porcelain industry in Kyushu would be the first option. In particular, the Yanbeta kiln, located in the Sotoyama area of Arita—that is, in the western part of the city where no strict control was exerted by the authorities on the production of certain types of porcelains—played a crucial role.

Consistent with the above-mentioned circumstances, shards in the Aode style have been found in the archaeological excavations carried out at the Yanbeta enameling kiln site [29,30]. The main characteristics of those scarce wares, fired right before the Yanbeta kiln was shut down in the late 1650s, were their unrefined style and coarse bodies [29,30,49]. The implication is clear: the last stage of production at Yanbeta was entirely focused on low-grade wares for the domestic market [49]. In this harsh environment and due to the strict limitations on the types of usable designs imposed by the authorities to protect the profitable porcelain business under the direct patronage of the Nabeshima clan, the Aode style, previously limited to Kaga and of no interest to the Nabeshima, formed the basis upon which Yanbeta potters tried to establish a new market. The attempt proved extremely expensive and unfortunately unsuccessful, as testified by the quality and limited number of shards excavated at the Yanbeta enameling kiln site, and a bitter end awaited: the Yanbeta kiln was shut down before long.

Skilled potters from Yanbeta, especially those experienced in overglaze enameling, had no option but to seek employment at the Aka-e Machi, the Enamellers' Quarter established in the late 1650s [29,49] by the Nabsehima clan in the Uchiyama area of Arita—the tightly-controlled central area where the core of the Japanese porcelain business was located. Their presence, on the basis of the results herein presented, finally explains the sudden appearance in Arita of a decoration style similar to the Kaga "Western-Style Painting on Porcelain": in order to meet the taste of the European aristocracy, a new stylistic approach based on the entire covering of the front of the wares, with some blank parts left on their underside, much like the Proto-Aode style, became systematically employed on a large production scale (Figure 41). The new Aka-e-Machi style, though, was almost uniquely realized using underglaze-blue decoration and red enameling (Figure 41), a much cheaper and easier-to-fire alternative than the fully enameled Ko-Kutani wares. The timeline of this innovative design shift in Arita is now clear: after Ko-Kutani production had ceased in Kaga in the latter half of the 1650s and the Yanbeta kiln had been shut down soon after, the Aka-e Machi (Enamellers' Quarter), established in the late 1650s, became the pole of attraction to Kaga and Yanbeta potters, who would now serve as the indispensable means by which the Nabeshima clan could exert a total control over the lucrative production of enameled porcelains.

(a)

Figure 41. *Cont.*

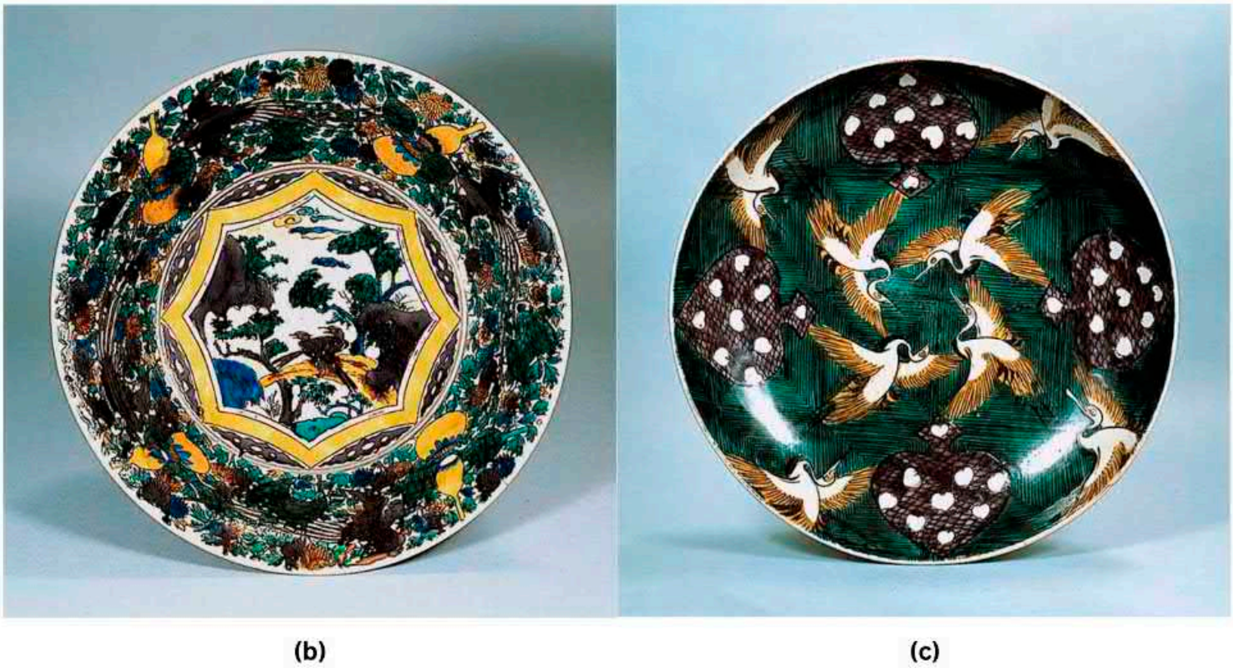


Figure 41. (**a**) Large dish for the European market (front and underside), decorated in underglaze blue and overglaze red and gold (*Kinrande* style), Arita, early 18th century (private collection); (**b**) Ko-Kutani *Scattered Flowers and Twin Birds* bowl (Collection of Ishikawa Prefectural Museum of Art); (**c**) Ko-Kutani *Karuta and Cranes* bowl (Collection of Ishikawa Prefectural Museum of Art).

Moreover, an additional benefit came from the implementation of the imported style: clay purification could be greatly reduced, because the gray tint of the body would basically be hidden by over-decoration (also discussed later). As a result, production could be increased to meet the demand of European merchants. Therefore, not only had the Aka-e Machi (Enamellers' Quarter) been established to improve the production process through better labor organization, but it also served as the place where production for the European market was extensively carried out from the late 17th century. This new timeline enables, for the first time ever, the identification of the Aode style as the source of inspiration that led Arita potters to develop the new European-oriented style of over-decorated wares employed at the Aka-e Machi, thus testifying to the transfer to Arita of the Western-based designs that had previously marked Ko-Kutani decorations in the Proto-Aode and Full Aode styles.

To conclude, the Aode style, after a short period of transregional and global relevance in 17th-century Japan, ended up lost to history. Fortunately, two centuries later, this precious heritage of the Maeda clan would be revived by the venture of the Yoshidaya kiln in Kaga in the early 19th century: the Aode style would be once again produced in the same geographical area of its origin and on the basis of its historic predecessor [50].

3.6. KO-KUTANI SHARDS—Ishikawa Prefecture Archaeological Foundation: Styles and Materials

Selected examples from the scarce shards excavated at Kaga kiln site A (Figure 42) were analyzed for the first time ever. A specific focus was placed on the overglaze enamels. The results are reported in the following sections.

Figure 42. Ko-Kutani shards: (**a**) Shard #310 (early-to-mid 1640s); (**b**) shard #493 (early-to-mid 1640s); (**c**) shard #22 (early-to-mid 1640s); (**d**) shard #595 (1652); (**e**) Kutani kiln, excavation site A (courtesy of Ishikawa Archaeological Foundation). Collection of Ishikawa Archaeological Foundation.

3.6.1. KO-KUTANI SHARDS—Overglaze Green—The Cu-Zn Connection

XRF spectra of the green enamels are reported in Figure 43. They all bear the Cu-Zn-based chromophore. What is striking is the perfect match between shard #310 and shard #493 (Figure 43, Table 3). The implication is clear: Kaga shards share the same green recipe identified on both Ko-Kutani porcelains fired in the Late Period and Nonomura Ninsei's wares.

Table 3. Cu/Zn ratios detected on the green enamels.

Element Ratio	*Shard #310*	*Shard #493*	*Shard #22*	*Shard #595*
Cu/Zn	19.07	19.76	10.68	12.04

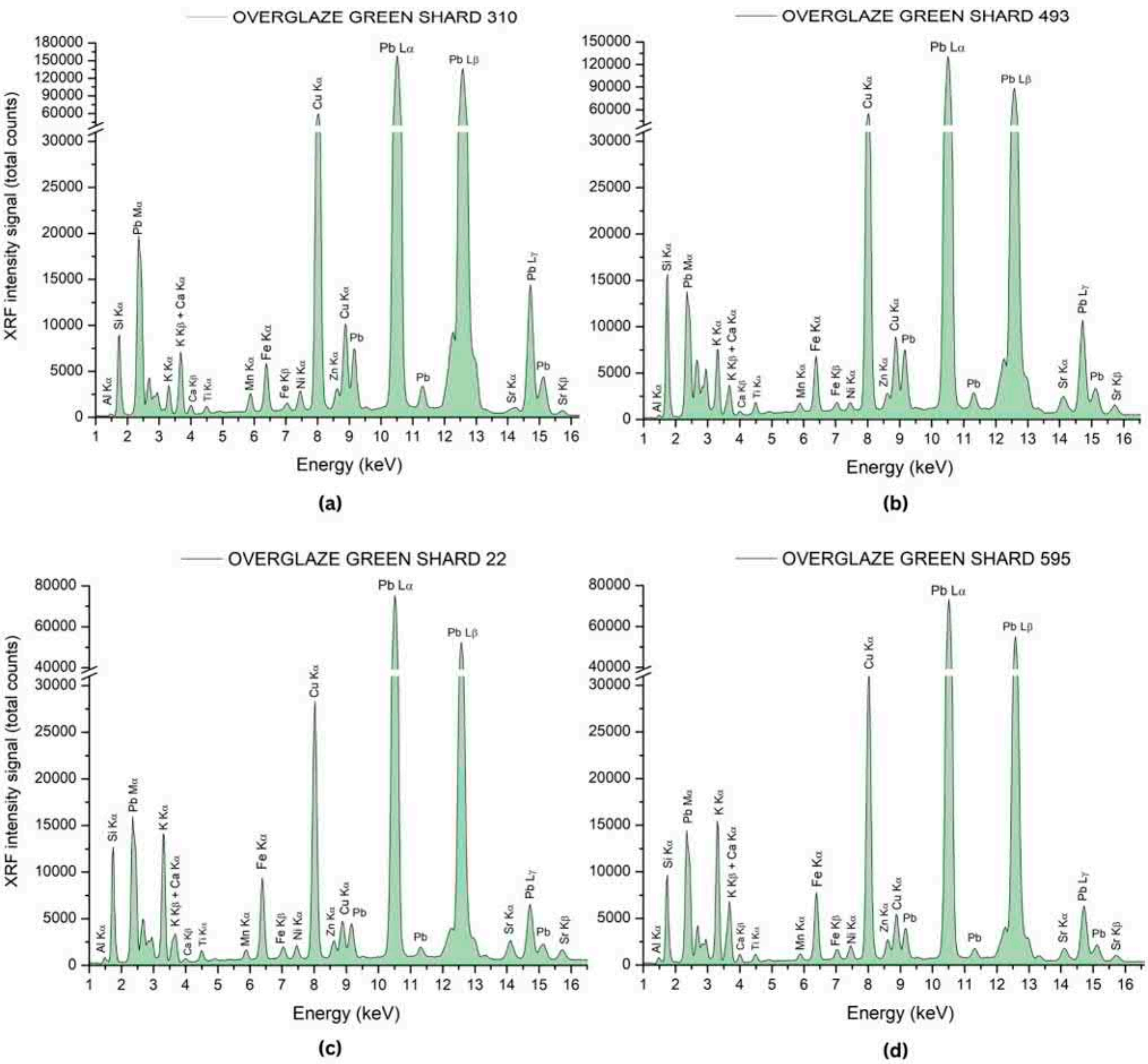


Figure 43. (ex 40) XRF spectra of the Cu-Zn-based green enamels detected on: (**a**) Shard #310 (early-to-mid 1640s); (**b**) shard #493 (early-to-mid 1640s); (**c**) shard #22 (early-to-mid 1640s); (**d**) shard #595 (1652).

Notable Matches: Green Enamel and Pigment

It is extremely relevant to report here the truly groundbreaking match between the Cu-Zn-based chromophore analyzed on shard #310 (Cu/Zn ratio of 19.07) and the Cu-Zn-based green pigment detected on the *Martyrdom of Leonardo Kimura* (1619) (Cu/Zn ratio of 18.38) (measurement point #P10 as indicated in the XRF spectrum) (Figure 44).

As in the case of Nonomura Ninsei in Kyoto (discussed in Section 3.1.2), the influence of the painting *Seminario* established in Japan by the Italian Jesuit painter Giovanni Cola in the late 16th century emerges from the continued transfer of materials and technqiues between Jesuit Missionaries and potters in Kaga.

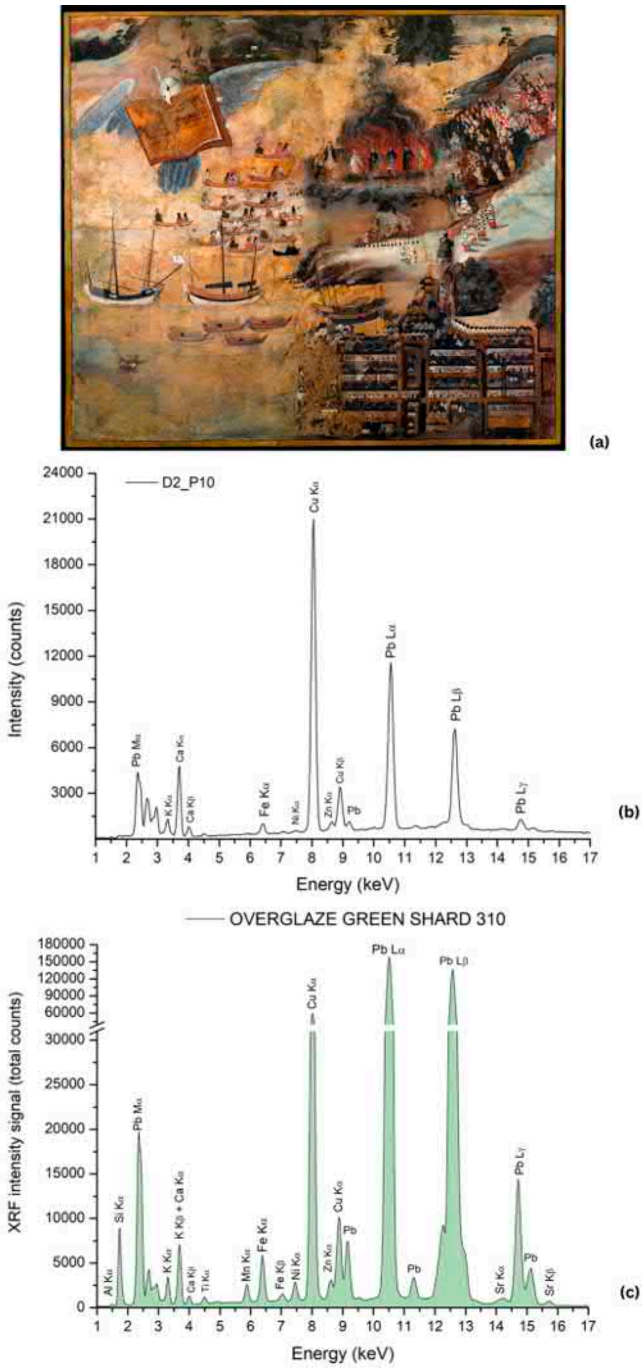


Figure 44. (**a**) *Martyrdom of Leonardo Kimura* (1619) (Collection of Chiesa del Santissimo Nome di Gesù all'Argentina, Rome, Italy); (**b**) XRF spectrum of the green pigment (Cu-Zn chemical composition) detected on the painting *The Martyrdom of Leonardo Kimura* (1619); (**c**) XRF spectrum of shard #310's overglaze-green enamel (Cu-Zn chemical composition).

3.6.2. KO-KUTANI SHARDS—Overglaze Blue—The Smalt Connection

XRF analysis of the blue decoration on shard #595 has allowed, for the first time ever, the identification of *Smalt* (Figure 45): the chromophore bears the characteristic chemical composition Fe-Co-Ni-As, with ratios of Mn/Co < 1 and As/Co between 0.35–0.50, trace to minor levels of Mn and noticeable levels of Cu—common in 17th-century *Smalt*—and no Cr [7–20]. Moreover, varying amounts of Fe, Co and Ni are consistent with both the expected variability of the element association in the cobalt ores sourced from the large deposits in the Erzgebirge region (Saxony) and Bohemia and the employment of different processing methods as by the historical records and geochemical data [7–21,25,37,38].

The implication is clear: the blue material detected on the shard, in terms of origin and recipe, proves perfectly consistent with the enamels analyzed on all Ko-Kutani porcelains and Nonomura Ninsei's wares in the Collection of the Ishikawa Prefectural Museum of Art (Sections 3.1.1, 3.1.2, 3.2.1 and 3.3.1). This first-time-ever evidence further confirms the transfer of European technology and materials to Kaga and the strong influence they exerted on Ninsei's development of overglaze enameling in Kyoto.

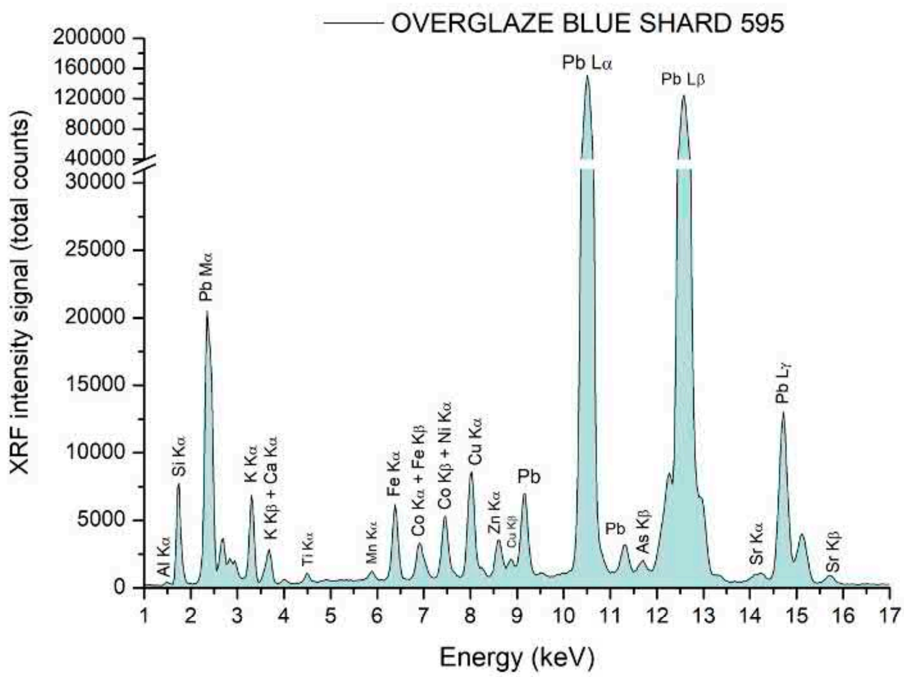


Figure 45. XRF spectrum of the overglaze-blue enamel (Fe-Co-Ni-As chemical composition with high K content) analyzed on shard #595.

3.6.3. KO-KUTANI SHARDS—Yellow Enamel

The yellow enamels analyzed on the Ko-Kutani porcelains in the Collection of the Ishikawa Prefectural Museum of Art and on the excavated shards all share the same Fe-based chromophore. Representative spectra from each of the three periods (Early, Middle and Late) and group of shards are reported in Figure 46.

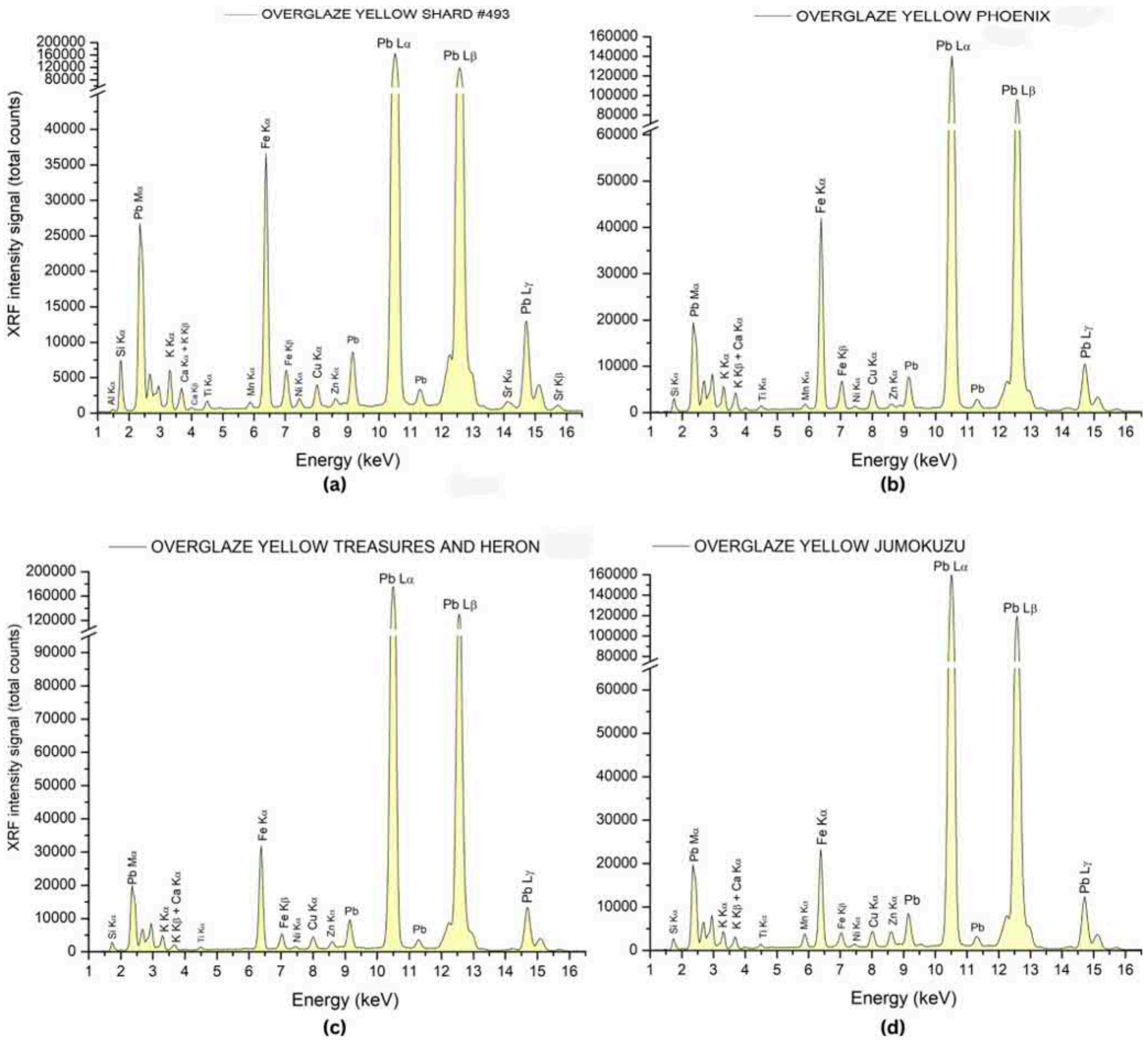


Figure 46. XRF spectra of yellow enamels: (**a**) Shard #493 (1640s); (**b**) *Phoenix* bowl (Early Period, 1648–1650); (**c**) *Treasures and Heron* bowl (Middle Period, 1650–1651); (**d**) *Jumokuzu* bowl (Late Period, 1654–1655).

The XRF intensity counts of Zn detected on the analyzed yellow enamels, as shown in Figure 47, fall within a narrow range of values. However, the overall consistency is faced with some obvious exceptions. Specifically, the bar graph reveals that the latter part of the Late Period (1653–1655) (light gray-colored bars) is marked by an increase in zinc in the enamel recipe. Furthermore, the *Scattered Treasure and Heron* bowl (lighter orange bar) (Middle Period) proves particularly interesting: its noticeable outlying zinc content, along with the presence of the Cu-Zn-As-based green enamel (Section 3.2.1), confirms its early firing. Also, a general dynamic behind porcelain production in Kaga is unveiled: period-to-period transitions were accompanied by thorough experimentations. As a result, in the latter part of the Late Period (1653–1655), the traditional translucent Fe-based yellow shifted to a more opaque and glossier type (richer in Zn) with more covering power, as by European practice [9]. XRF analysis has enabled, for the first time ever, the identification of the timeframe within which the recipe was actually developed, along with the Kaga potters' ingenuity in making each recipe instrumental to the introduction of new decoration styles.

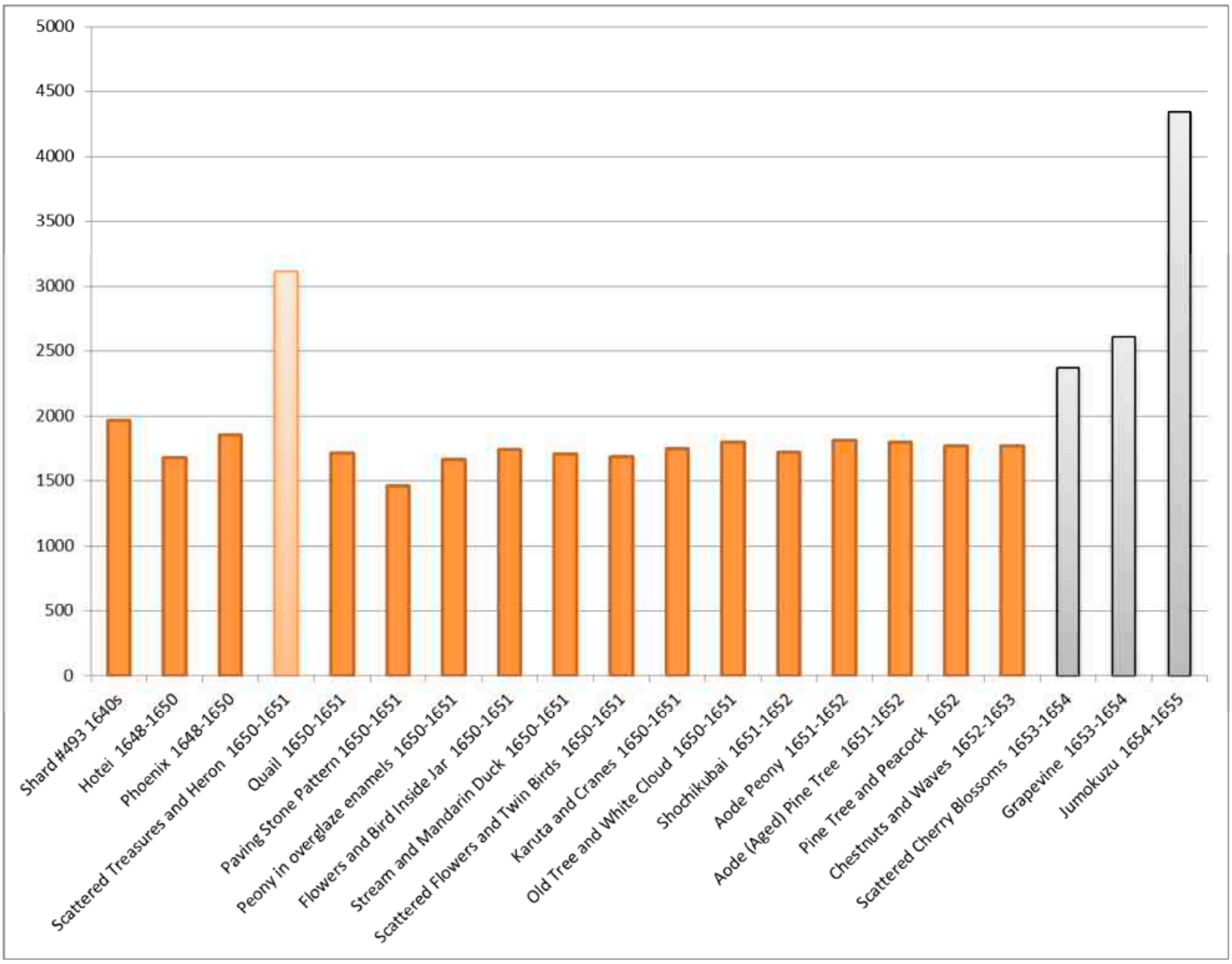


Figure 47. XRF intensity counts of Zinc detected on the analyzed yellow enamels in all three periods of Ko-Kutani production.

3.7. KO-KUTANI SHARDS—Glazes

3.7.1. Glazes—Initial Experimentation and the Early Period (1648–1650)

XRF analysis has revealed that the glaze recipe, following the inception and development of different Ko-Kutani decoration styles, underwent different changes over a small period of time. The analytical technique has shown that an extensive experimentation was carried out by Kaga potters in order to produce a glaze type that would enhance the visual impact of overglaze enamels. The earliest attempts, represented by shards #310, #493 and #22 (mid-1640s), featured a basically transparent glaze obtained by the mere addition of botanic ash to the clay used for the body, with Rb/Sr ratios of 0.19, 0.28 and 0.29, respectively (Table 4, Figure 48). Such a recipe, in perfect agreement with the production of Arita wares (Shoki-Imari) [27], confirms the initial influence of potters from Kyushu, as discussed in Section 3.1.1 (Movement of Potters, Technological Transfer and Design Development). Moreover, XRF analysis has revealed that this early glaze type was decorated with the same Cu-Zn-based green enamel identified on Ninsei's wares (Section 3.1.2) and with a translucent Fe-based yellow.

Table 4. Ratios of Rb and Sr detected on the glazes of the excavated Ko-Kutani shards.

Element Ratio	Shard #310	Shard #493	Shard #22	Shard #595
Rb/Sr	0.19	0.28	0.29	0.45

The following step, as testified by the analysis of the *Hotei* bowl (Early Period, 1648–1650), was the application of the Cu-Zn-As green enamel on an opaque and subdued white glaze characterized by an Rb/Sr ratio of 0.81 (Section 3.1.1). The incorporation of the more expensive *Smalt*-based blue enamel followed immediately after, as observed on the *Phoenix* bowl (1648–1650), which, as in the case of the *Hotei* bowl, bears the same opaque and subdued white glaze with an Rb/Sr ratio of 0.9 (Section 3.1.1). The implication is clear: the transition from the initial experimentation (shards #310, #493 and #22; mid-1640s) to the firing of the full-fledged Ko-Kutani enamels in the Early Period (1648–1650) involved a substantial change in glaze recipe. Potters switched from the Arita-based transparent glaze type (Rb/Sr ratios of 0.19–0.29) to a more opaque and subdued white glaze type (Rb/Sr ratios of 0.81–0.9).

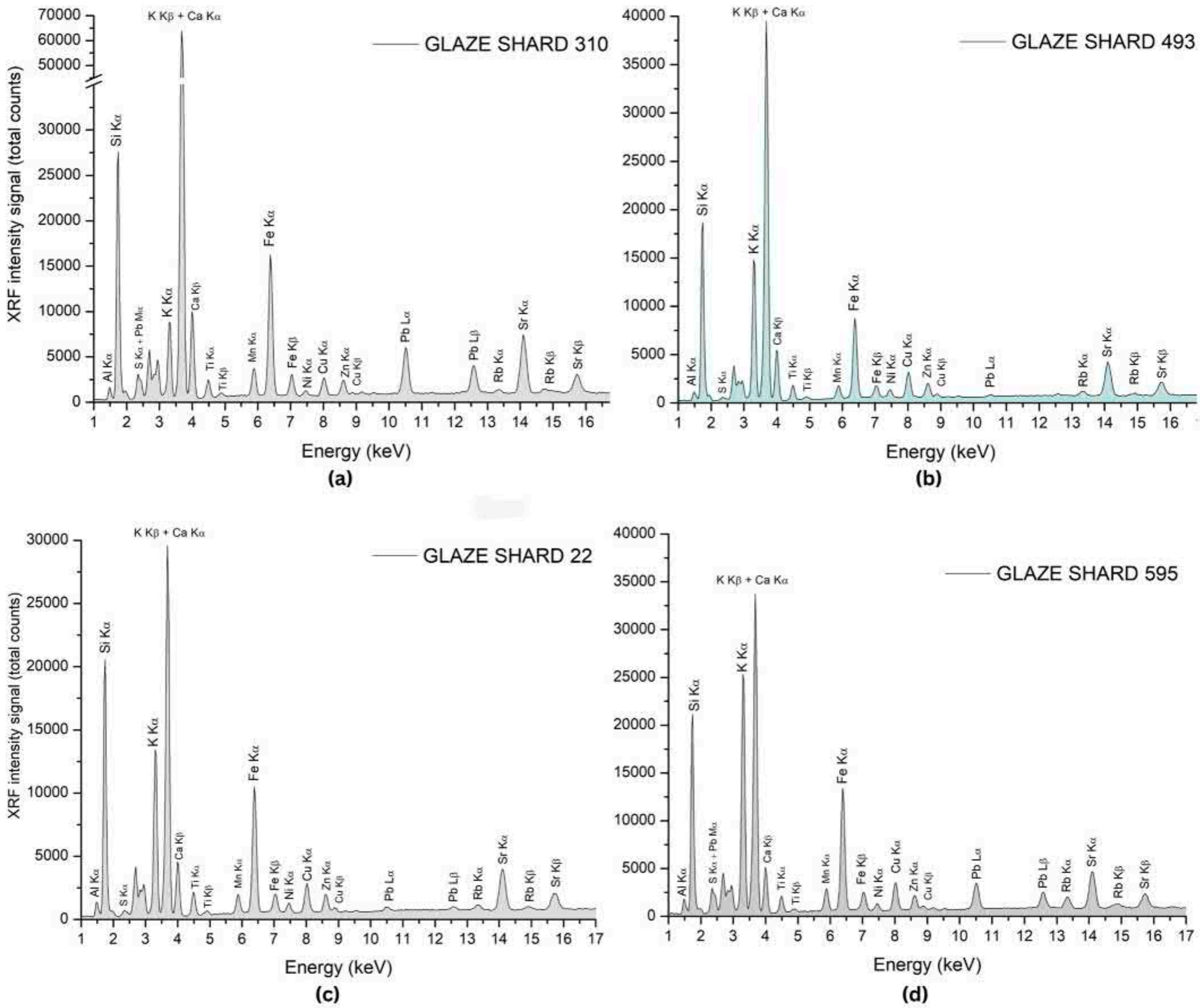


Figure 48. XRF spectra of glazes: (**a**) Shard #310; (**b**) shard #493; (**c**) shard #22; (**d**) shard #595.

3.7.2. Glazes—The Transition from the Early Period to the Middle and Late Periods

As the European-inspired Aode style was being brought to life in the Middle Period (1650–1651), a further step-based glaze shift took place in Kaga. The bar graph in Figure 49 shows that as the traditional and restrained type of decoration of the Early Period (1648–1650) (Section 3.1.1) was being progressively replaced by the European-based practice of covering the entire body with enamels (Section 3.2.1), a gradual decrease in the Rb/Sr ratio partially reversed the previous technical process: Rb/Sr ratios switched from the initial 0.8–0.9 range to values of around 0.8–0.6 in the Middle period (1650–1651) and 0.45 in the Late Period (1651–1655).

Two obvious exceptions show nearly identical outlying Rb/Sr ratios: the *Scattered Treasures and Heron* (Rb/Sr ratio of 0.43) (Middle Period) and the *Old Tree and White Cloud* (Rb/Sr ratio of 0.44) (Middle Period) bowls. As previously discussed, these two have been identified, for the first time ever, as transitional pieces, Early-to-Middle and Middle-to-Late, respectively. The implication is clear: a methodical experimentation process had been devised by Kaga potters to introduce major style changes in porcelain decoration. Therefore, not only is the *Scattered Treasures and Heron* bowl (Rb/Sr ratio of 0.43) one of the earliest Ko-Kutani wares fired in the Middle Period, but it also served as the starting point for the development of a group of recipes (glaze and enamel) that would deeply influence technical experimentation in later transitional phases, as testified by the *Old Tree and White Cloud* bowl (transitional Middle-to-Late-Period example, Rb/Sr ratio of 0.44) and shard #595 (Late Period piece, Rb/Sr ratio of 0.45).

To conclude, the shift to the Full Aode style in the Late Period (1651–1655) led potters to focus entirely on enameling. As a result, the glaze lost the role of background enhancer it had played in the Early Period (opaque glaze—Rb/Sr ratio of 0.8–0.9) and became merely instrumental to the newly developed decoration scheme (transparent glaze—Rb/Sr ratio 0.45).

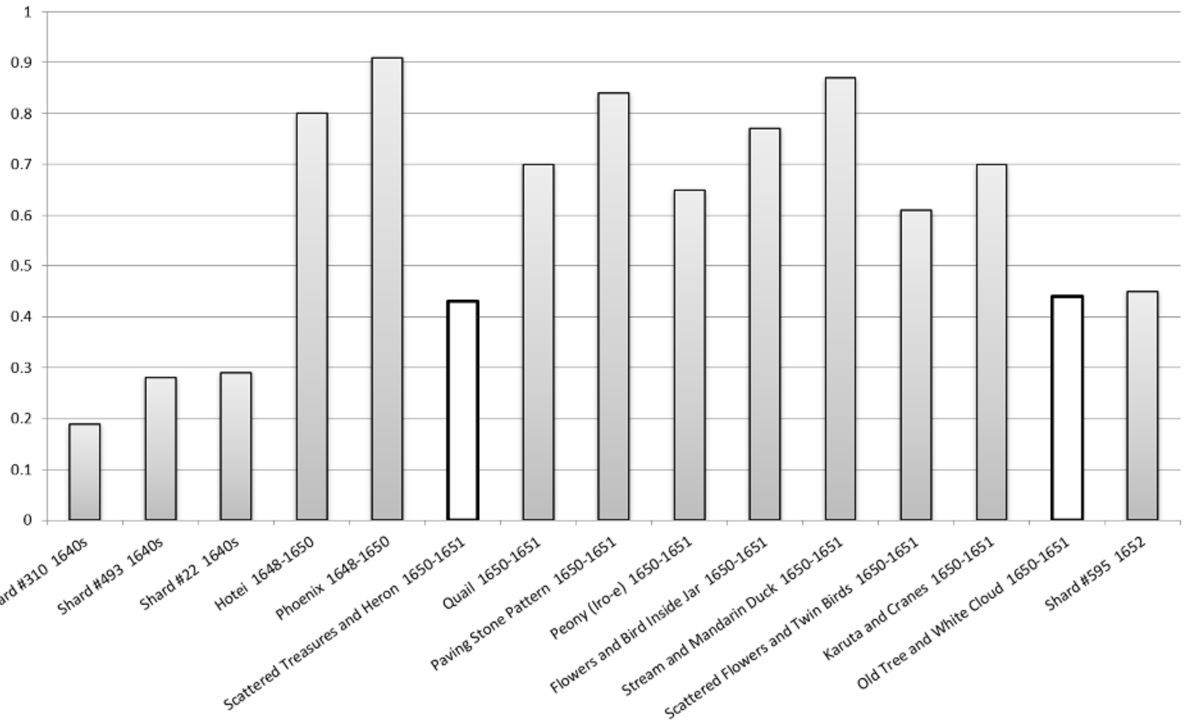


Figure 49. Rb/Sr ratios in all three periods of Ko-Kutani production, including the excavated shards.

3.8. KO-KUTANI SHARDS—Bodies

The analyzed shards are characterized, on average, by high contents of Ti and Sr (Figures 50 and 51). This first-time-ever evidence points to the use of a local clay and sets apart Ko-Kutani bodies from the low-Sr and low-Ti ones fired in Arita, as observed by Montanari [27]. Moreover, the bar graph in Figure 51 provides a new insight into material processing in the Late Period (1651–1655): the significantly higher Ti content detected in the body of shard #595 reveals that the practice of covering the entire wares with overglaze enamels had led potters to reduce the labor-intensive purification process of the clay to cut costs, the grayish tint caused by the presence of Ti in the body being no longer visible (discussed also in Section 3.5.2). This instance is perfectly consistent with both the overall reduced use of costly blue enamel decoration and the shift from the Cu-Zn-As green chromophore used in the Early and Middle periods to the Cu-Zn-based coloring agent employed for Full Aode decoration and Ninsei's wares. The results, therefore, unveil that cost-cutting practices had become essential in the last period of Ko-Kutani production, affecting bodies and enamels alike.

To conclude, the following significant points need to be emphasized here. The scarce shards of misfired bodies excavated at the Kutani kiln site suggest that Arita potters, although provided with a slightly different type of clay, managed to successfully transfer to Kaga the basic potting and glazing techniques developed in Kyushu [27]. On the reverse side, in the second half of the 17th century, Arita potters employed cost-cutting practices inspired by the Kaga potters' experience (Section 3.5.2): a shortened clay purification process coupled with an extensive decoration of bodies with underglaze-blue pigment and red enamel, thus incorporating aesthetic principles that had actually originated in Kaga but that later became the drivers of Arita's exports to Europe (Figure 41).

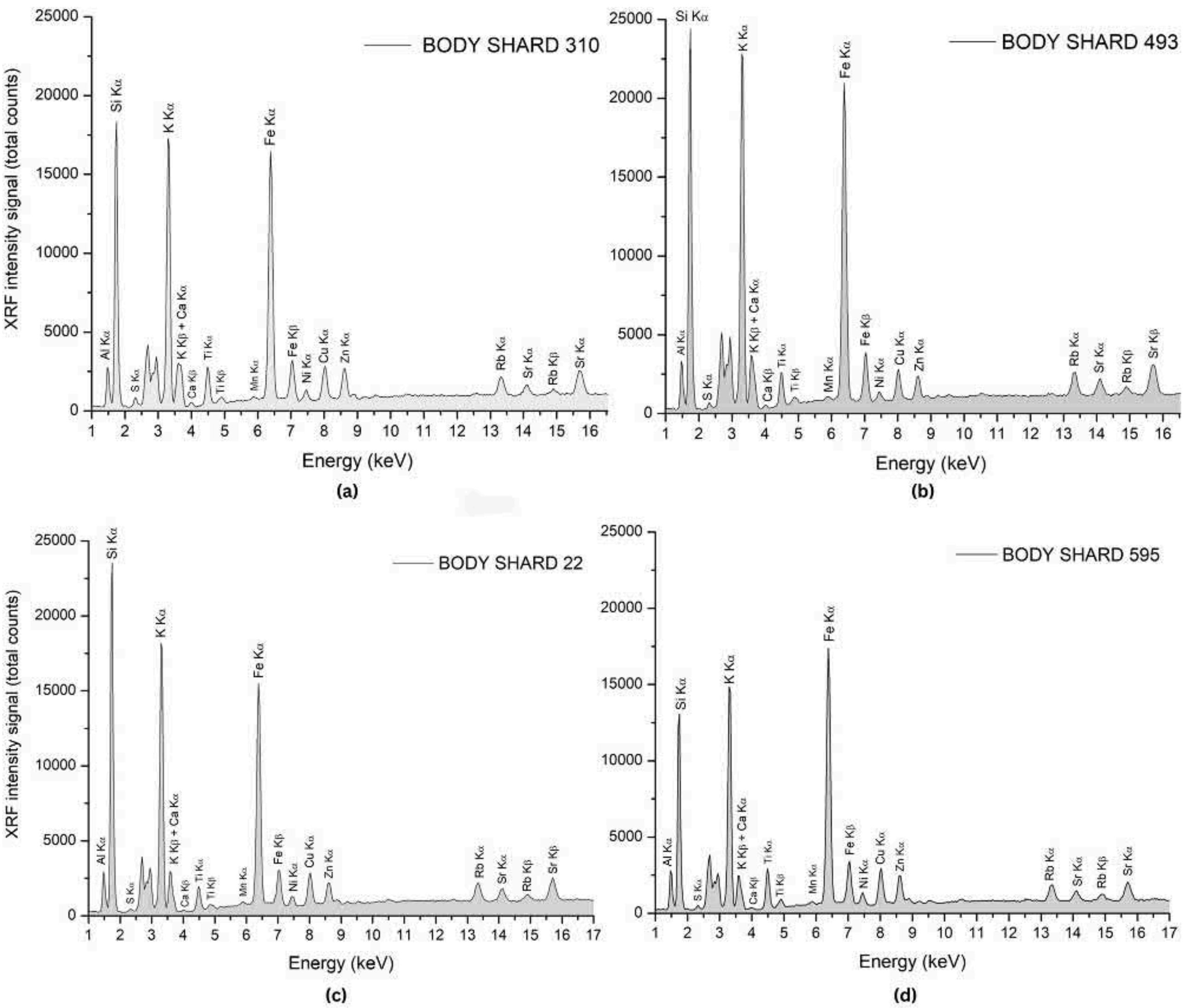


Figure 50. XRF spectra of bodies: (**a**) Shard #310; (**b**) shard #493; (**c**) shard #22; (**d**) shard #595.

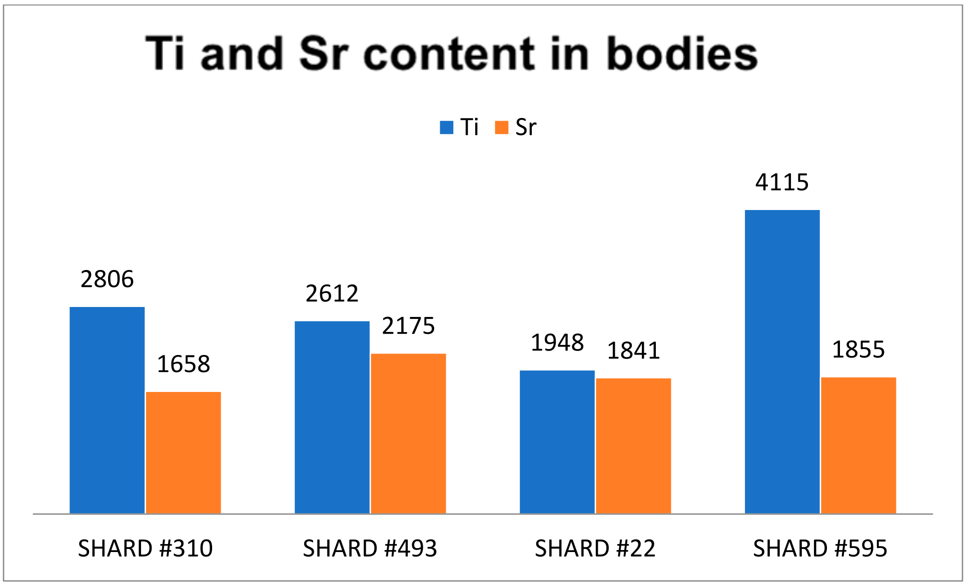


Figure 51. Bar graph of the Ti and Sr XRF intensity counts detected in the bodies of the excavated shards.

4. Conclusions

XRF analysis has enabled, for the first-time-ever, the identification of both the production process of Ko-Kutani porcelains and the timeline by which Ko-Kutani and Ninsei's wares can be dated on scientific and stylistic grounds. Three main periods, Early, Middle and Late, are characterized by the use of specific glazing and enameling materials.

The potting and glazing techniques in Kaga have proven to be the result of potters settling in the Maeda fiefdom after their expulsion from Arita in 1637, while enameling has proven to be the result of the crucial influence exerted by European technological practices introduced by Jesuit Missionaries in Kaga.

European *Smalt* played an absolutely key role, as it was uninterruptedly employed as a ready-to-use material for blue enameling since the very inception of Kutani wares, and it consistently accompanied the development of the iconic Proto-Aode and Full Aode styles. In order to best suit such changing decoration styles, glaze recipes underwent a thorough experimentation.

The analytical evidence has revealed that Nonomura Ninsei and the Kaga potters benefitted from the same technological transfer by Jesuit Missionaries as in the Maeda fiefdom, as testified to by the early and efficient use of European *Smalt*, by the employment of the same Cu-Zn-based green enamel also detected on 17th-century Italian ceramics and paintings and by Ninsei's innovative application on porcelain of the European cold gilding technique.

The results have also unveiled the inception of the Full Aode style, a groundbreaking novelty that was brought to life by merging European painting practices and enameling on porcelain, thus giving birth to the first "Western-Style Painting on Porcelain" in the Far East, a technique that would also impact Arita porcelain production for the European market from the late 17th century onward.

Author Contributions: The research project was conceived by R.M., H.M. and R.M. prepared the manuscript. The shards were selected by H.M. and R.M. The analyses were carried out by R.M. The results were interpreted by R.M., M.F.A., S.S. and H.M., C.P. and M.F.A. also revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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