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European *Smalt* in 17th-Century Japan: Porcelain Decoration and Sacred Art

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Abstract: Japanese art tradition, contrary to the case of China, is characterized by an efficient and continued, although mostly undocumented, use of *smalt* from the late 16th century onward. Recent studies have successfully identified this pigment, the cobalt-colored glass that spread throughout the Old Continent during the Renaissance period, as the coloring agent employed for overglaze-blue enameling on Japanese porcelains produced at the kilns of Arita (the porcelain production center of Japan) from the early 1640s until the 20th century. Fragmentary evidence of the use of *smalt* in Japanese sacred art has also been reported, yet its earliest incorporation into such a type of traditional art form could not be identified. In order to resolve this crucial issue, portable EDXRF was employed for the non-destructive analyses of Japanese porcelains and sacred images bearing blue decoration. Scientific analysis allowed, for the first time ever, to establish a clear timeline of *smalt* use. Furthermore, this evidence and the literature data both agree, leading to the identification of the origin of the blue material used on both art productions.

Keywords: *smalt*; Jesuit; Arita; Buddhist art; sacred art; enamel; porcelain; Yanbeta

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1. Introduction and Historical Context

Japanese art tradition, contrary to the case of China, is characterized by an efficient and continued, although mostly undocumented, use of *smalt* from the late 16th century onward [1–4]. This European cobalt-colored glass rich in potassium that spread throughout the Old Continent during the Renaissance period [5,6] has recently been discovered to have been the chromophore employed for overglaze-blue enameling on Japanese porcelains produced at the kilns of Arita (the porcelain production center of Japan) from the early 1640s until the 20th century [1,2].

Previous studies on Japanese Buddhist works of art [7–9] have only provided fragmentary evidence of the use of *smalt* in sacred art, thus failing to identify the timeline of its introduction and earliest use.

European pigments started being imported into Japan by the Italian Jesuit painter Giovanni Cola, who arrived at Nagasaki from Rome in 1583 at the request of Alessandro Valignano, the supervisor of the Jesuit Mission [1–4,10]. Father Cola established the first painting *Seminario* (painting school) in the Far East after his arrival in the country. *Arie*, located in Kyushu, the southernmost main island of the Japanese archipelago, hosted the *Seminario* from 1595 to 1597. Giovanni Cola himself established a glass workshop in *Arie* in 1595 [11] under the patronage of the Christian Samurai *Naito Tokuan Johan*, friend of *Takayama Ukon*, making such a place the first full-fledged hub of Renaissance technology.

Not only had painters who trained at the *Seminario* used newly imported European pigments such as *Arie Black* [3], but the influence of the glass technology transferred at *Arie* led, as we will see later on, to the early incorporation of *smalt* into Japanese sacred art in the late 16th century [3,7–9].

The production of the painting *Seminario* focused mainly on sacred images, as they were a very effective means by which the new religion could be taught to the Japanese and Chinese alike. Due to the fierce persecutions that followed the ban on Christianity promulgated by the Tokugawa Shogunate in 1614, a ban that was finally lifted in 1873 as a result of the diplomatic pressure exerted by Western powers trading with Japan during the Meiji period (1868–1912). No written records survived the two-hundred-and-fifty-year-long prohibition. Any traces of the interaction between the Japanese and the missionaries during the Christian century (1549–1639) were intentionally destroyed. Had any connection to Christianity, even a vague one, been found by the authorities, torture and death would have been an unavoidable fate; therefore, the Japanese burned or hid any such records from that period [12].

Moreover, due to the harsh persecutions, Giovanni Cola was forced to flee to Macau (China) from Nagasaki in 1614, where he reunited with his two pupils (painters), Jacob Niwa and Emanuel Pereira, who had studied and trained at *Arie* before going back to China in the late 16th century to support the Mission of Father Matteo Ricci [3,4,13].

The results herein presented enabled the identification of the earliest introduction and use of *smalt* in Japanese sacred art, thus establishing a definitive timeline where all the fragmentary pieces of evidence available so far can be consistently placed to unveil an unknown chapter of Japanese history.

2. Materials and Methods

2.1. Artifacts

All the analyzed shards were provided by the Arita Museum of History, Arita, Saga Prefecture, Japan, and were excavated at the Yanbeta kiln site in Arita (Table 1). They date to the early 1650s. Yanbeta has recently been identified as the kiln where overglaze enameling on porcelain started in Japan in the 1640s [14,15]. The shards had never been analyzed prior to this study.

Table 1. Characteristics of the analyzed shards excavated at Yanbeta kiln site.

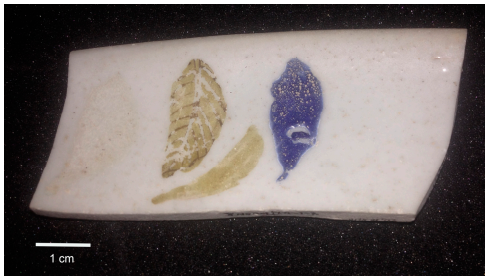
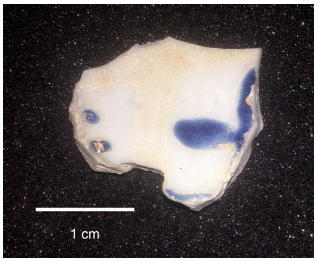
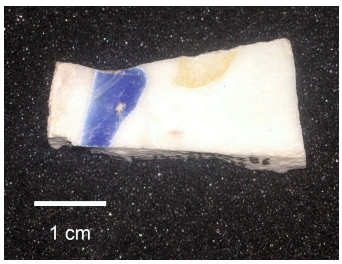
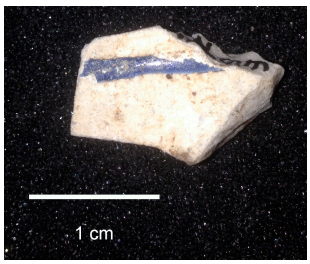
Kiln Site	Shard	Technology	Date
Yanbeta (shard Y1)		Polychrome overglaze decoration	Early 1650s
Yanbeta (shard Y2)		Polychrome overglaze decoration	Early 1650s

Table 1. *Cont.*

Kiln Site	Shard	Technology	Date
Yanbeta (shard Y3)		Polychrome overglaze decoration	Early 1650s
Yanbeta (shard Y4)		Polychrome overglaze decoration	Early 1650s

Buddhist Sculpture

The analyzed sculpture, from a private collection, depicts *Amida Nyorai* (Buddha) standing on a lotus base (Figure 1a). The wooden figure, lacquered and gilded, was made using the *Yosegi-Zukuri* (assembled pieces) [16] technique in a workshop located in present-day Kyoto prefecture. The head is painted with a bluish pigment, as is common in Japanese practice for such Buddhist representations. We were fortunate to be allowed to analyze it, as it bears an inscription with the date of the 7th year of the *Genroku* period, corresponding to the year 1694 (Figure 1b).



Figure 1. (**a**) Buddhist sculpture depicting Amida Nyorai (height 55 cm); (**b**) inscription with the date 1694.

2.2. XRF Spectrometer: Experimental and Measurement Parameters

The employed XRF portable instrument consists of a miniature X-ray tube system, which includes the X-ray tube (max voltage of 40 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 (SDD) with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line Energy Resolution (depends on peaking time and temperature); a 1 keV to 40 keV Detection range of energy; a max rate of counts to 5.6×10^5 cps; software for acquiring and processing the XRF spectra.

Primary beam and detector axis form an angle of 0 and 40 degrees, respectively, with the perpendicular to the sample surface. Measurement parameters were as follows: tube voltage 35 kV; current 80 μA, acquisition time 100 s; no filter was applied between the X-Ray tube and the sample; 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 (SNR). A comparison of the spectra on a peak-by-peak basis has been carried out [17].

XRF analysis has been widely employed in conservation sciences and archaeometry on the basis of its capability to efficiently, and in a non-destructive way, identify many chemical elements (with atomic numbers higher than sodium $Z > 11$) in a single measurement of the investigated surface, combined with instrument portability.

The complexity of the chemical matrices and stratigraphic sequences of archeological/historical/artistic materials has made quantitative analysis of anisotropic heterogeneous matter a difficult task when sampling (in particular, the preparation of a polished section in order to analyze each layer) is not permitted, and results are basically to be considered semi-quantitative even with a supposedly homogeneous matrix or known stratigraphy.

In the case of chromophore identification, 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 marker chemical elements. In fact, this technique has been successfully and efficiently applied to layered samples: Cesareo et al. and Trojek et al. evaluated both the thickness and depth of distribution of chemical elements in multilayered structures by measuring Ka/Kb, La/Lb and La/Lg X-ray ratios in pigment layers in paintings and gilded or silvered alloys [18–20] (depths of element calculation is available online at "https://xrfcheck.bruker.com/InfoDepth (accessed on 6 April 2024)".

The present study has employed such a methodological approach and has provided objective parameters by which *smalt*-based blue coloring agents on selected Japanese porcelains and sacred-art objects could be compared, all through the systematic analysis of the X-ray K-line ratios of the marker elements of *smalt*, specifically As-Co, Mn-Co, and Co-Ni.

It is well known that the intensity ratio becomes higher as the layer thickness increases because the attenuation coefficient of the Ka (La) line is larger than that of the Kb (Lb) line.

To conclude, considering both the similar chemical matrices of the analyzed blue layers and the similar intensity values detected on the same typology of chromophores for all XRF spectra, the same characteristic peaks are directly comparable for each of the analyzed layers, along with the intensity ratios of As, Mn, Co, and Ni.

3. Results and Discussion

3.1. Cobalt-Rich Ores, Saffre and Smalt

It is important to remark here that Co^{2+} ions are the main coloring agent in a silicate blue glass; the other techniques, Cu^{2+} ions in Egyptian blue and Han blue, lapis lazuli (La Téne and Roman glass, Ptolemaic blue, then Iranian, Norman and Mameluk blue) and modern blues (V:Zr) were only used at specific times [21–26].

Before the 17th century, cobalt itself was not considered a valuable chromophore as the origin of its name suggests, that is, the bad demon *cobolt* to which it referred due to the great toxicity caused by its association with arsenic in the Erzgebirge silver mines [22]. In the exploitation of silver, the associated elements (mainly Si, As, Co, Bi, Cu and Ni from European mining sources [27]) were found in the slag, which alone or diluted in glass was

called saffre. From the 16th century, with the development of printing, bismuth was used to harden lead, and hence the content of Bi in *saffre* decreased. At the same time, for the blue coloring of paper but also for the enamels of earthenware and majolica, cobalt was exploited by itself, and different grades of *smalt*—a *saffre* optimized/improved by mixing with the potassium glass of Bohemia containing about 10 to 20% CoO—was produced and marketed mainly by the Dutch [28–31].

The Asian geological context around the Himalayas is very different from that of the old European Hercynian massifs (hydrothermal veins), and the Asian cobalt sources (association of transition elements Fe-Mn-Co-(Ni)) are characterized by the associations of very different elements that make it possible to differentiate the origins of the cobalt. The identification of the elements associated with Co, in particular Mn, As, and K, will therefore be a criteria for discussing the origin of the 'cobalt' used. On the technical level of enameling, the Co-As association proves advantageous as arsenic in sufficient quantity in a glass containing lead precipitates in an opacifying white phase, which enhances the color [21].

3.2. Yanbeta Porcelain Kiln: The First Systematic and Large-Scale Use of Smalt in Japanese Art Production

The XRF spectra of the blue enamels analyzed on the Yanbeta Y1, Y2, Y3, and Y4 shards (Y4 will be thoroughly discussed in Section 3.3) (Figures 2–5) all show the characteristic fingerprint of European *smalt*: the chemical composition Fe (Kα)-Co (Kα)-Ni (Kα)-As (Kβ) with ratios of Mn/Co < 1 and As/Co between 0.35–0.50 [1], trace to minor levels of Mn, noticeable levels of Cu—common in 17th-century *smalt*, and no Cr [1,2,5,32–46]. Striking is the similarity between the Fe-Co-Ni-As *smalt* detected on the Japanese shards and the composition of the Fe-Co-Ni-As *smalt* identified on an Italian dry-painted low relief dated 1506 [32].

The Fe-Co-Ni-As element association and the As/Co signal ratios point to both Skutterudite $(Co,Fe,Ni)As_{2-3}$, the most important cobalt ore from Saxony, characterized by varying amounts of the elements Fe, Co, and Ni with a resulting variability in the Fe-Co-Ni-As composition [33,40], and/or Cobaltite (Co,Fe)AsS as frequently suggested [5,7,47,48].

Moreover, along with the above-mentioned matching chemical compositions, the high peak intensity of K detected on all blue enamels, be it Japanese porcelains or European ceramics, firmly confirms the use of *smalt*.

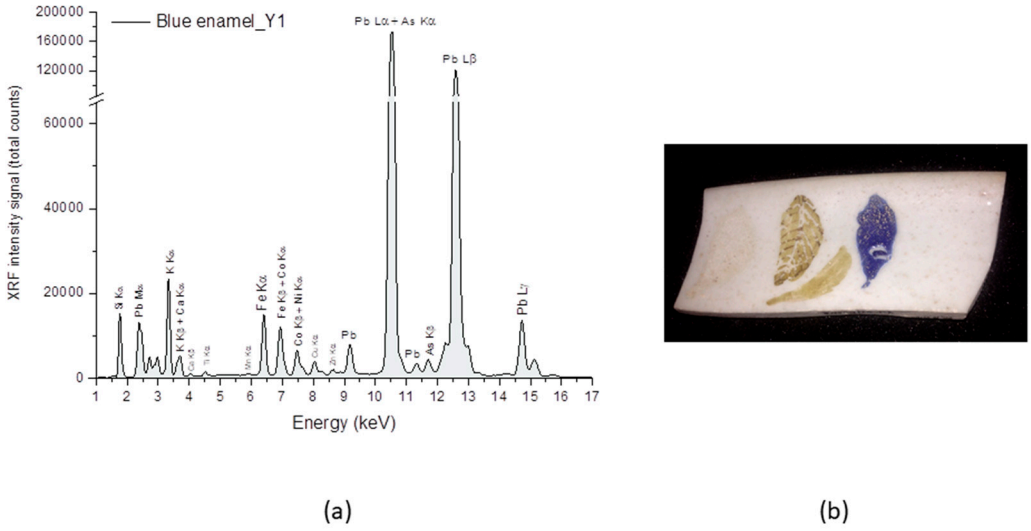


Figure 2. (**a**) XRF spectrum of the blue enamel analyzed on shard Y1; (**b**) Shard Y1.

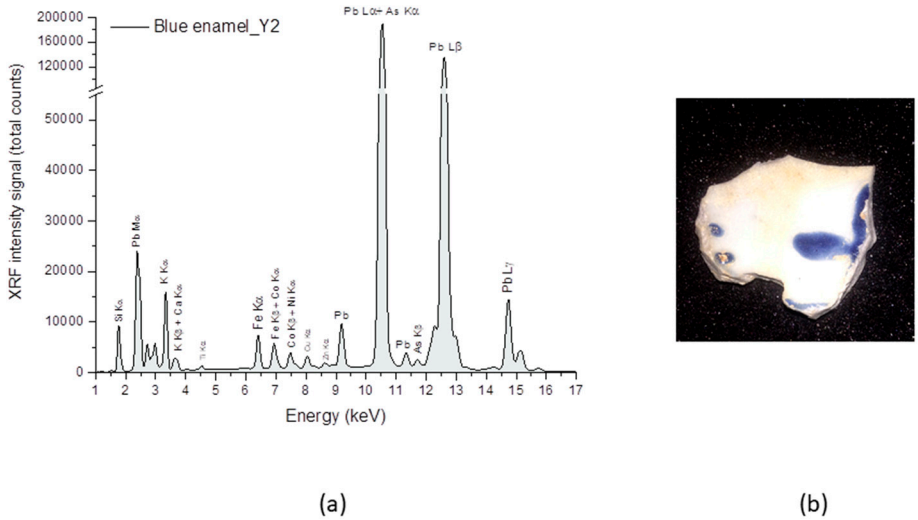


Figure 3. (**a**) XRF spectrum of the blue enamel analyzed on shard Y2; (**b**) Shard Y2.

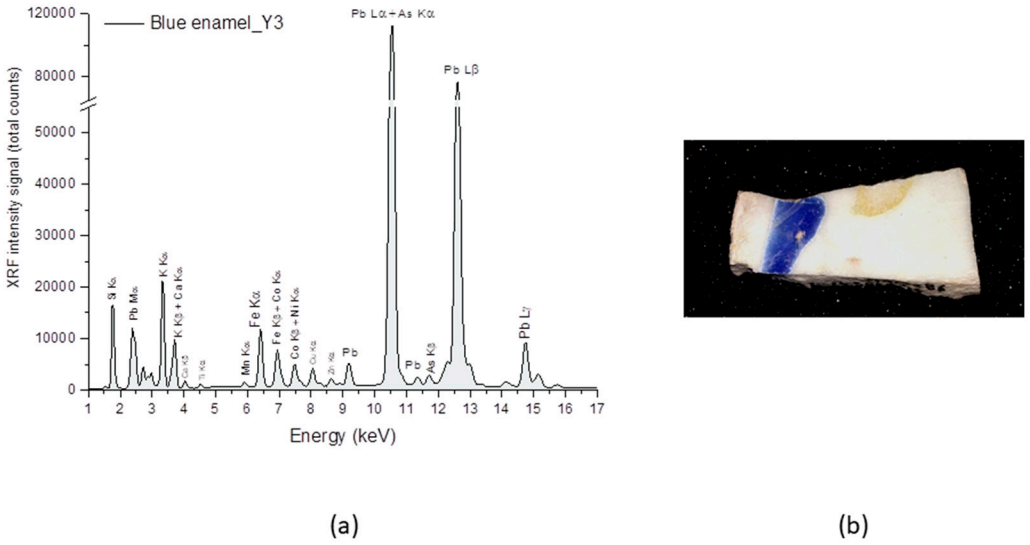


Figure 4. (**a**) XRF spectrum of the blue enamel analyzed on shard Y3; (**b**) Shard Y3.

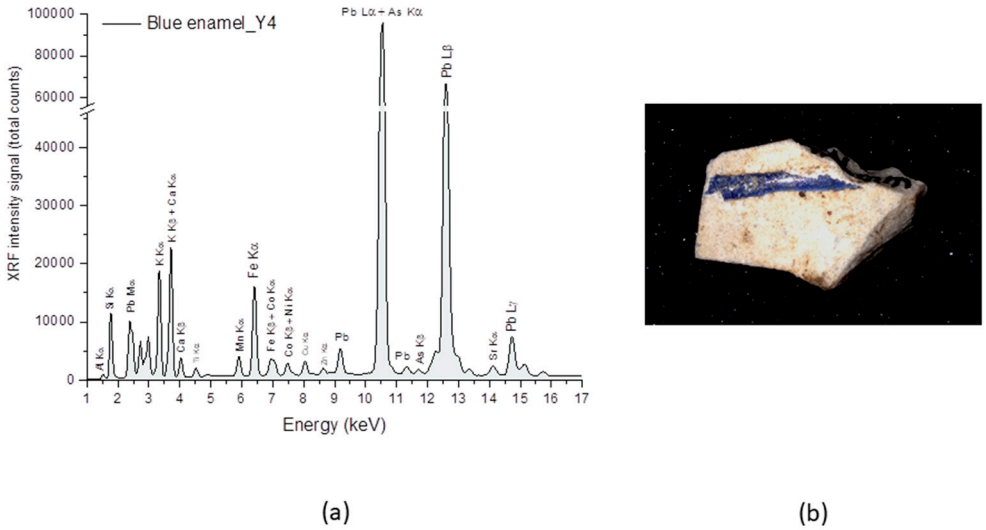


Figure 5. (**a**) XRF spectrum of the blue enamel analyzed on shard Y4; (**b**) Shard Y4.

Extremely relevant is to remark here that the results presented in this work, as shown in Table 2, are in perfect agreement with those reported in previous studies for both the unmixed and mixed (the mixed pigment is discussed in Section 3.3) blue pigments used in Japan for porcelain decoration from the early 1640s [1,2]: European *smalt* bearing the chemical composition Fe-Co-Ni-As, commonly used throughout the Renaissance period in Italy and Europe [1,2,5,32–40,45,49–51] proves to have been the cobalt ore used from the earliest phase of overglaze-blue-enameling development in Arita.

Table 2. Ratios relating to unmixed *smalt* used in different period of porcelain production in Arita.

Period of Production	Mn/Co **	As/Co **	Technique
1640–1650 (shards Y1,Y2,Y3)	<1	0.35–0.50	Unmixed blue pigment
1640–1650 *	<1	0.50–0.60	Unmixed blue pigment
1660–1670 *	<1	0.40–0.65	Unmixed blue pigment
1670–1700 *	<1	0.35–0.53	Unmixed blue pigment

* Adapted from [1]. ** Mn(Kα), Co(Kα), As (Kβ) [the stronger As(Kα) line overlaps with the Pb(Lα)] are indicated with tags in the XRF spectra reported in the figures.

The consistency of the Fe-Co-Ni-As element association observed on the overglaze-blue-decorated porcelains fired throughout the 17th century in Arita [1,2], along with the As/Co and Mn/Co ratios, strongly point to cobalt ores sharing a common geochemical origin and/or processing method: such compositional characteristics are in line with the *smalt* obtained from Europe and made available to Italian potters and painters by Venetian glass makers in the 15th century [33,34,48].

Furthermore, the *smalt* used on 16th-century Venetian paintings served as a cheaper substitute for more expensive pigments (lapis lazuli and natural ultramarine) in 17th-century Italian paintings [5].

It is noteworthy to report here the compelling compositional similarity of the Fe-Co-Ni-As blue enamel used throughout the 17th century to the chemistry of the pigments used in Japan on porcelain and sacred art. A very notable instance comes from Shimoyama and Noda, who firmly identified the Fe-Co-Ni-As chromophore on an important votive painting dated 1682 [7]. Furthermore, a Japanese Buddhist sculpture depicting *Tamonten* [9] bears the same element association for the blue pigment (Table 3).

Table 3. Chemical composition of blue pigments detected in Japanese sacred art.

Period of Production	Sacred Art (Media and Technique)	Blue Composition
17th century	*Tamonten* Japanese Buddhist sculpture Polychrome pigments on wood	Fe-Co-Ni-As
1682	*Rashoumon-zu* Japanese votive painting (*Ema*) Polychrome pigments on wood	Fe-Co-Ni-As

It is worth mentioning that Japanese potters and painters will continue to import *smalt* from Europe until the early 20th century, when the Meiji policy of strong westernization of the country will lead to the establishment of a full-fledged state-of-the-art industry with the incorporation of preparative chemistry [52] for the industrial production of purified chemical compounds such as carbonates, sulfates, nitrates, or oxides. Japan had become once again, after four hundred years, the hub for European materials and technology in the Far East [2].

Furthermore, the use of the same pigments for both paintings and ceramics belongs to European technical practices and is not part of the Japanese artistic tradition [1,2,10].

3.3. Origin of the Japanese Mixed-Blue Pigment: The Yanbeta Enameling Workshop

The spectrum of the blue enamel analyzed on Y4 (Figure 5) is characterized by a chromophore bearing a higher amount of Mn and lower amounts of Co and As than Y1, Y2, and Y3. Such chemical composition reveals the use of a mixed-blue pigment, that is, a European-*smalt*-based coloring agent to which a low-grade cobalt ore was added [1]. This mixed-blue pigment, embedded in a Pb-rich matrix for overglaze decoration, has been successfully identified by Montanari on Arita porcelains produced in the latter half of the 17th century and destined for the European market [1,2] (Figure 6). Such wares were characterized by heavy decorations that would cover most of the porcelain bodies, an effective technique that required a considerable amount of blue material to be applied. In order to improve profits, Japanese potters started to systematically employ the innovative and cheaper mixture as soon as the export trade with Western countries commenced in the latter half of the 1650s, not long after the establishment of the *Aka-e machi* (the enamelers' quarter) located in the eastern *Arita—Uchiyama* area, where all skilled potters had been gathered by the authorities to exert strict control over the entire production process [1,2].



Figure 6. Porcelain shard (1660–1670) excavated at the *Aka-e machi* (enameler's quarter) site in Arita. Fired for the European market with overglaze decoration covering most of the body. The blue color is a mixture of *smalt* and a low-grade cobalt ore [1], such as the pigment detected on Y4.

The earliest incorporation of the mixed-blue pigment into porcelain making was therefore thought to have been the result of a thorough experimentation with European materials carried out at the *Aka-e machi* (the enamelers' quarter) in the mid-1650s. Yet, the analysis of shard Y4 has led to a groundbreaking discovery: the mixed-blue pigment had already been developed and used by Yanbeta potters in the late 1640s to early 1650s, way before the establishment of the *Aka-e machi* and the commencement of the trade with Europe. The implication is clear: Yanbeta potters had been tirelessly experimenting with European materials under the supervision of Jesuit missionaries in the earliest phase of overglaze-enameling development [1,2,10]. The systematic and large-scale use of the mixed-blue pigment to produce export wares at the *Aka-e machi* in the latter half of the 1650s [1] was the result of the transfer of the new technology by Yanbeta potters. This crucial discovery confirms what has been a mere speculation until the present work: Yanbeta potters had actually moved to the *Aka-e machi* after their kiln had been shut down in the mid-1650s due to unfavorable business conditions, namely, lack of patronage from the Nabeshima authorities; thus, transferring to enamelers at the *also known as-e machi* the skills and knowledge they had previously acquired from Jesuit missionaries from the late 1630s [1,10].

The first-time-ever evidence of the European origin of the mixed-blue pigment employed for the development of overglaze-blue decoration on Japanese porcelains comes from our analysis of a majolica dish fired at Deruta in the early 17th century (Figure 7). The XRF spectrum of the blue enamel (Figure 7) reveals the use of *smalt* bearing a high content of Mn to obtain a different shade of color. The comparison between Y4 and the Italian enamel provides a remarkable match (Figures 5 and 7; Table 4).

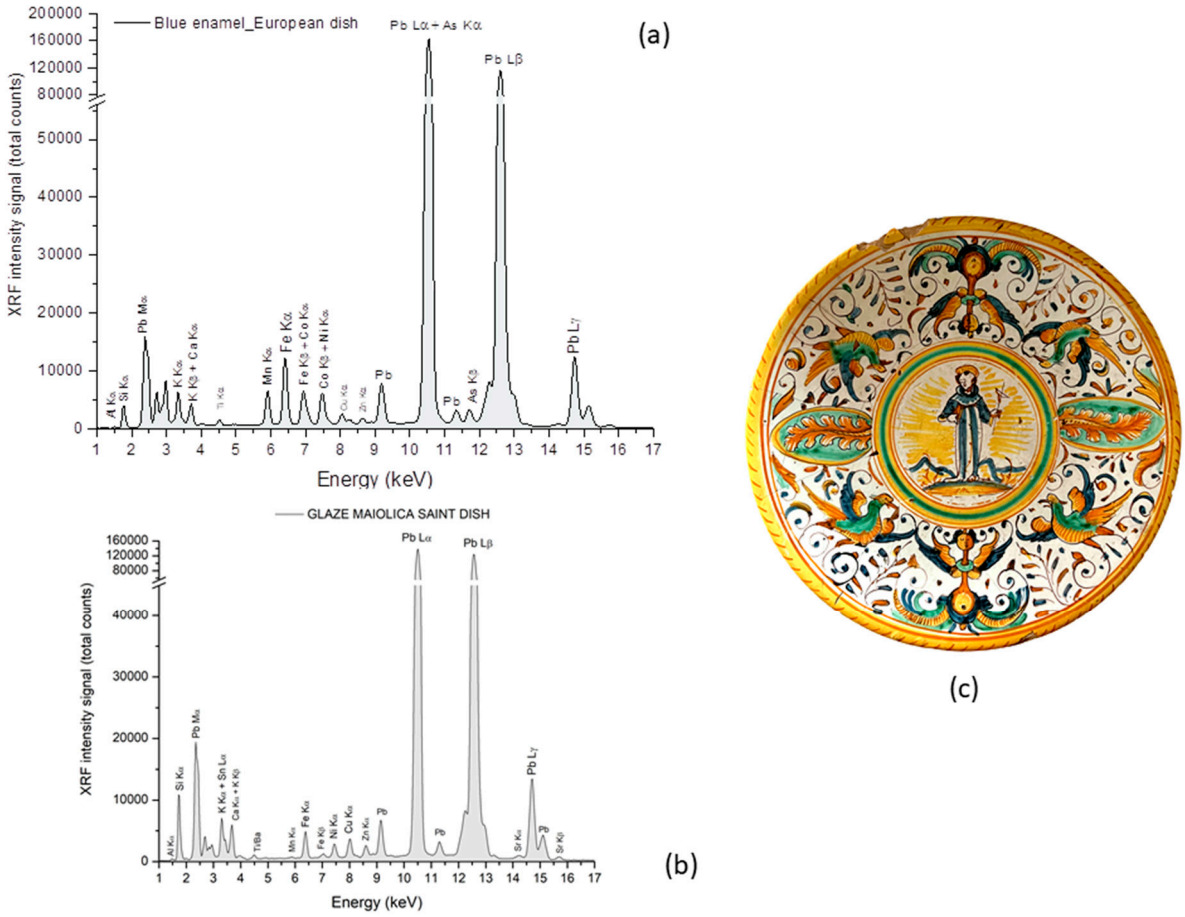


Figure 7. (**a**) XRF spectrum of the blue color analyzed on the Italian overglaze-enameled majolica fired at Deruta kilns, 1600–1650 (private collection); (**b**) XRF spectrum of the glaze; (**c**) Italian majolica dish fired at Deruta.

Table 4. Ratios relating to *smalt*-based mixed blue pigments used in different geographical areas in the 17th century.

Period of Production	Mn/Co	As/Co	Technique	Composition
1640–1650 (Yanbeta kiln, Y4)	1.09	0.50	Mixed blue pigment	Fe-Co-Ni-As-Mn
1600–1650 (Deruta kilns, Italy)	0.98	0.50	Mixed blue pigment	Fe-Co-Ni-As-Mn
1650–1670 * (also known as-e Machi)	1.4–2.4	0.48–0.56	Mixed blue pigment	Fe-Co-Ni-As-Mn

* Adapted from [1].

The variation in the Mn/Co ratios indicates that after the first experimentation with European blue materials carried out by Yanbeta potters in the late 1640s to early 1650s—clearly demonstrated by the nearly identical values detected on Y4 and the majolica fired at Deruta in Italy (Table 4), the original European recipe underwent subtle changes in the latter half of the 1650s at the *Aka-e Machi* (the enamelers' quarter): additions of progressively higher amounts of Mn marked enamel production in order to obtain a cheaper pigment for the decoration of export wares destined to the European market.

The implication is clear: the use of the mixed-blue pigment for porcelain decoration in Japan was the result of the technological transfer from Italian Jesuit missionaries to Yanbeta potters in the 1630s. The new scientific evidence casts further light on the technological influence exerted by European practices on Japanese art from the late 16th century onward.

3.4. Deruta and Venetian Blue Pigments: The Italian Connection

Cobalt-based pigments from Erzgebirge (Saxony) and Bohemia were available to glass factories in Murano (Venice) at least from the 13th century [48]. During the Renaissance period, Italian potters obtained *smalt* through Venice [48], as confirmed by scientific analyses carried out on sculptures by Della Robbia [47,48] and on majolica wares produced at Deruta [49], Casteldurante [35], Gubbio [38,49], Caltagirone [37], and Faenza [35,48] from the 15th century [37,38,45–49].

Analytical evidence, therefore, points to Italy as the predominant agent through which the use of *smalt* spread throughout Japan in the late 16th and early 17th centuries. This distinctive dynamic proves consistent with the role Italy has already played in Europe in the late 15th and 16th centuries, when the emigration of Italian potters to Portugal, Spain and northern Europe led to the transfer of majolica technology [48,53].

Venetian glass-based blue (Murano glass technology) and shards excavated at the Yanbeta enameling kiln-site, including the examples presented in this study, all bear the same element association Fe-Co-Ni-As [1,2,34,38,47,48]. This crucial evidence strongly points to the glass workshop established in *Arie* (Kyushu) by the Italian Jesuit painter Giovanni Cola in 1595 [11] as the hub of *smalt* distribution in Japan. The implication is clear: Italian Missionaries had managed to establish an early transfer route to the country in the late 16th century in order to enable the creation of sacred images and secular paintings at the local *Seminario*. Such artistic and religious endeavors were further strengthened by the development of an actual trade route under the direct control of Portuguese merchants, whose presence had become a crucial contributor to the establishment of a full-fledged trade channel between Europe and Japan. Most likely, the Venetian glass materials requested by Giovanni Cola for local use were exported from ports in Portugal, where blue-decorated azulejos were gaining popularity [30], thus promoting an inter-European trade that also involved countries in northern Europe, i.e. Holland, where the production of Saxony-and-Bohemia-*smalt*-based pigments had also started [21].

This distinctive and profitable dynamic, which had also exerted a deep technological and social influence on the process of reunifying Japan under Oda Nobunaga [54], lasted until the enforcement of the harsh persecutions by the Tokugawa shogunate in the late 1630s [12,54]. After the *sakoku* (isolation) policy went into effect, causing Japan to close to the outside world with all Jesuits and Christians expelled from the country in 1639, the trade ended up becoming a monopoly of protestant Dutch merchants [1,2,21], thus losing its religious and cultural focus to turn into a mere lucrative exchange. The incident of the slaughter of the Portuguese-Embassy members sent to Japan in 1640 to negotiate the reopening of the trade between Portugal and Japan, a killing that had been ordered by the Tokugawa shogunate, provides a definitive testament to how the new anti-Christian policy had irreversibly changed the Japanese social environment. The Christian century that had started under the full support of Oda Nobunaga in the mid-16th century came to a bitter end under Tokugawa Ieyasu [12,54].

3.5. Blue Pigment on Amida Nyorai's Head: European Influence on Japanese Sacred Art

The chemical composition of the blue pigment detected on the head of the Buddhist sculpture (Table 5; Figure 8) provides new evidence of the use of European *smalt*. The high intensity of the As and Co peaks indicates that the blue layer consists of the pigment applied to an organic medium.

Table 5. Chemical composition of blue pigments detected in Japanese sacred art.

Period of Production	Technique	Composition
17th century [9]	Japanese Buddhist sculpture	Fe-Co-Ni-As
1682 [7]	Japanese votive painting	Fe-Co-Ni-As
1694 Amida Nyorai [herein presented]	Japanese Buddhist sculpture	Fe-Co-Ni-As-Bi

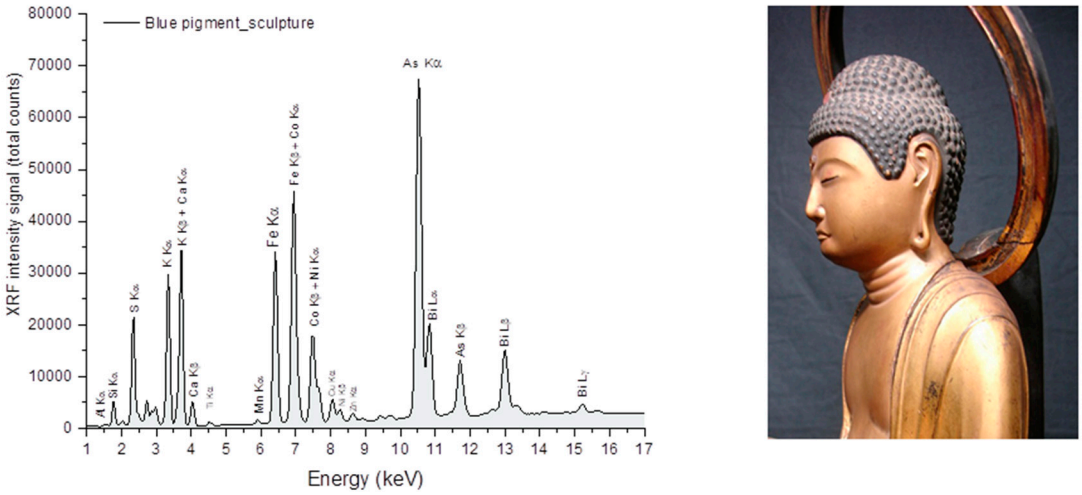


Figure 8. (**a**) XRF spectrum of the blue enamel analyzed on the head of the Buddhist sculpture; (**b**) close-up of the sculpture.

The coloring agent is characterized by the Fe-Co-Ni-As-Bi element association, which is characteristic of cobalt-ore sources from the Erzgebirge region as determined by historical records and geochemical data [21,36,47,50,51]. The presence of Cu, trace to minor levels of Mn, no Cr, and a ratio of Mn/Co < 1 are perfectly consistent with Renaissance blue material [1,2,5,7,32–40,50,51]. Furthermore, the As/Co ratio of 1.47 fits perfectly into the range of values identified on European ores, that is, 0.76 to 4 [35,37,47].

As previously remarked, the use of the same pigments on different media, belongs to European technical practices and is not part of the Japanese artistic tradition [1,2].

The new evidence herein presented shows that in the late 17th century, besides the predominant availability of the Venetian Fe-Co-Ni-As *smalt*, a European Fe-Co-Ni-As-Bi blue pigment made its appearance. The presence of bismuth, one of the most volatile components along with Arsenic, may well be explained by the expected compositional variations that occur within a single large deposit and/or the change in material processing [34,36,38]. Not to be ruled out is the direct supply of *smalt*-based blue pigments by the Dutch as part of an overall strategy aimed at further strengthening their trade monopoly with Japan and influence within Europe, thus explaining the different element associations occasionally detected on the exported material in the late 17th century.

4. The Introduction of *Smalt* and the Timeline of Its Use throughout the Edo Period (1603–1868) on Different Media

Historical and Scientific Perspective

From a historical perspective, the analytical evidence provides firm grounds that allow us to unveil, for the first time ever, an unknown chapter of Japanese history. It has now become possible to fully comprehend the deep roots European technology had into Japanese society, to the extent that even sacred art ended up being strongly influenced by Western materials well beyond the Christian century (1549–1639). The results also help identifying a clear timeline for the introduction and use of the European blue pigment on the different media.

As mentioned in Sections 1 and 3.4, *smalt* was imported for the first time by the Italian Jesuit painter Giovanni Cola after his arrival in Japan in 1583. The Jesuit Father supervised the establishment of a glass workshop in *Arie* in 1595 [11], and soon after, *smalt* (*Arie Blue*) spread throughout the country [7–9].

From a scientific standpoint, until this work, previous evidence of the use of *smalt* in sacred art was basically overlooked or ignored due to the lack of a consistent framework.

We can now establish such a framework as all the unrecorded pieces of this historical and scientific puzzle go into place perfectly.

The present findings, in full accordance with recent evidence [1,2], have identified and confirmed the employment of *smalt* as a widespread chromophore for overglaze blue enameling on Japanese porcelains produced at the kilns of Arita (the porcelain production center of Japan) from the mid-1640s [1,2].

Moreover, *smalt* was successfully detected on a late-16th-century hand-colored Buddhist print [8], on a 17th-century Buddhist statue of *Tamon Ten* [9] (Table 5), on a highly important votive painting (*Ema*) dated 1682 [7] (Table 5), on Ukiyo-e paintings from the late 17th to the 19th century—including Ogata Korin's *Flowers and Rocks* (late 17th century) [5,55], and a work by Utamaro (early 18th century) [5]. Even though the results were strongly pointing to an extensive use of the European material in different media, there were no written records of any such practice. Still, evidence was clearly suggesting that the expensive pigment was the primary choice for the production of high-grade works of art that would serve as formal and devotional offers to the Japanese elite and local temples and shrines.

Further proof of the broad circulation of *smalt* in Japan throughout the Edo period (1603–1868) comes from the *Kaishunsai* paints, an early 19th-century collection of pigments belonging to the Nabeshima family [56]. The pigments are stored in Takeo city, located in Saga prefecture, in the vicinity of Arita, where the development of overglaze-blue decoration on porcelain started in the 1640s based on the *smalt*-based enamel imported by the Jesuits [1,2].

The Nabeshima family had a crucial role in the control of production and kiln organization in Arita, so the presence of *smalt* in the clan's material collection [56] further testifies to the influence of European technology on art production in Japan throughout the Edo period.

Additional important confirmation of the uninterrupted circulation of European *smalt* comes from the maps of Japan based on the surveying of the famous cartographer Tadataka Ino (1745–1811): the maps date to the early 19th century and bear a blue decoration based on the Fe-Co-Ni-As-Bi *smalt* from Europe [57]. Moreover, *Doro-e* pictures produced from the mid-18th to the 19th century using western perspective and to be viewed through European optical devices have recently been discovered to have been painted using the Fe-Co-Ni-As *smalt*-based blue pigment [58].

The fragmentary scientific findings have basically been outlining a timeline that can now be fully understood and summarized: the *Seminario* in *Arie*, with the establishment of the glass workshop in 1595 under the supervision of the Italian Jesuit painter Giovanni Cola [11], served as the earliest place of introduction of *smalt* in the late 16th century [1–3,11]. The vitreous blue pigment exerted a strong influence on Japanese art right after it had become available, as testified by its detection on the late-16th-century hand-colored Buddhist print [8]. Moreover, *smalt* proved essential for the development of overglaze blue enameling on porcelain from the early 1640s [1,2], and became extensively incorporated into sacred art, *ukiyo-e* paintings, and folk art from the late 16th century onward [5,7–9,55–58].

It is relevant to mention here that European pigments supplied to the Jesuit *Seminario* in Japan were also incorporated into Chinese art in the early 1600s by painters who had trained in Japan in the 1590s under the supervision of the Italian Jesuit painter Giovanni Cola [3]. Moreover, European materials such as *smalt* started being systematically used for porcelain decoration at Jingdezhen (the porcelain production center of China) in the early 1700s, after the emperor Kangxi had ordered the Jesuits to establish a glass workshop in the Imperial Palace in 1695 [59–61]. China, therefore, will essentially follow the same path that Japan had successfully explored in *Arie* one hundred years earlier [1–3,59]. A very important conclusion can be drawn here: the glass workshop, wherever established, served as the crucial facility where Jesuit Missionaries introduced European technology and materials to new territories.

5. Conclusions

XRF measurements prove that *Smalt* made its appearance in Japan after the arrival of the Italian Jesuit painter Giovanni Cola from Rome in 1583 and the establishment of the first Jesuit painting *Seminario* in the Far East (Arie, Kyushu, Japan) in the early 1590s.

The use of the blue material bearing the element association Fe-Co-Ni-As spread throughout the country and influenced art production on different media, be it prints, porcelain, Buddhist sculptures, or votive paintings. Venetian masters started using the cobalt material imported from Saxony-Bohemia at their glass factories in Murano (Italy) in the early 14th century, so it is finally clear how the establishment of the first Jesuit glass workshop in Asia by Giovanni Cola at Arie (Kyushu, Japan) in 1595 was a direct consequence of the Italian influence on local art practices at the educational facilities of the Mission in Japan.

XRF analyses on the porcelain shards fired at Yanbeta kiln have provided, for the first time ever, the definitive evidence that Italian technology influenced enamel decoration in Arita from its earliest stage of development: the innovative incorporation by Japanese potters of the Venetian-*smalt*-based blue enamel and the mixed-blue pigment utilized at the kilns of Deruta for the decoration of Italian majolica during the Renaissance period took place in Arita around the late 1630s to early 1640s.

As testified by the Fe-Co-Ni-As-Bi chemical composition, European companies (i.e., Dutch merchants) that traded with Japan after the ban on Christianity in 1639 continued to be the dominant supplier of the blue material throughout the centuries. The newly detected presence of Bi is most likely related to the expected compositional variations that occur within a single large deposit and/or the change in material processing throughout the decades of the late 17th century.

Non-destructive spectroscopic techniques have proven to be an indispensable tool for research to develop further, allowing for new evidence to unveil unknown chapters of Japanese history and discover places where the Eastern and Western civilizations successfully met.

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