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SEM STUDY OF BLACK, BLUE, VIOLET AND YELLOW INGLAZE COLOURS OF THE OLDEST SWISS TIN-OPACIFIED STOVE TILES (*C*.1450–*C*.1512, CANTON BERN)**

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The ceramic colours of eight late medieval to early Renaissance stove tiles were studied by scanning electron microscopy-backscattered electron (SEM-BSE) images and SEM with energy-dispersive spectroscopy (SEM-EDS). Microstructural observations and chemical compositions of these colours give some insight into the colouring agents and techniques used by the potters. All decorations were applied as inglaze opaque colours on the unfired powdery tin-opacified glaze. The base glass was a Si-Pb glass, that is, for the blue, not a K-rich smalt. Two Co blue, with or without relics of Fe-Co-Ni and Ni-Co spinels ('safre'), could be distinguished. Pb-Sn-Sb triple oxide was used for the yellow. The violet was obtained by adding some Mn to the tin-opacified glaze. The black was either a Mn-doped blue or a CuO-SnO_2 black. The colours were probably purchased and not locally prepared.

KEYWORDS: LATE MEDIEVAL–EARLY RENAISSANCE STOVE TILES, SWITZERLAND, INGLAZE COLOURS, SEM-EDS

INTRODUCTION

Late medieval to early Renaissance tin-opacified stove tiles in Switzerland are the first witnesses of the introduction of this peculiar glazing technique on such objects. They account for only a few per cent of the vast number of shards recovered in archaeological excavations. Archaeological finds from Bern, Fraubrunnen, Fribourg, Zug and Zurich were extensively studied from the point of view of their dating, shape, decoration and manufacturing technique (Schweizer 1990; Roth Kaufmann *et al*. 1994; Boschetti-Maradi *et al*. 2004; Bourgarel 2007, 2013; Frey 2016). The present study is a complement to Maggetti (2020), who analysed the bodies, slips and glazes of 14 tin-glazed stove tile fragments from Bern, Fraubrunnen and Nidau. The focus lies on the microscopic and microchemical identification of the colorants used for the inglaze paintings of these oldest Swiss tin-glazed stove tiles in order to understand the recipes and manufacturing technique used.

MATERIALS AND METHODS

The eight fragments studied (Table 1 and Fig. 1) were part of the archaeological assemblages excavated in Bern (Roth Kaufmann *et al*. 1994), Fraubrunnen (Schweizer 1990) and Nidau (Boschetti-Maradi *et al*. 2004).

The colorants used were determined by scanning electron microscopy (SEM). For this process, small cross-sections were cut from the objects at the permitted locations using a diamond saw.

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Table 1 *Selected samples*

An. no.	*Date**	*Provenance and year of excavation*	*Description*	*Reference*
Ofe 43	1443–1513? (1450–75)	Nidau, Hauptgasse 32, town hall, 1993	Fragment of a flat cornice tile. Reddish body. White slip. White, opaque tin glaze. Decor: inglaze, square bosses and garland motif in grey-blue, yellow, black. Length of the upper edge = 6 cm	Boschetti-Maradi *et al*. (2004), cat. 20, fig. 18 (Lnr. 27055, Fnr. 46804-3)
Ofe 44	1443–1513? (1450–75)	Nidau, Hauptgasse 32, town hall, 1993	Fragment of a flat cornice tile. Reddish body. White slip. White, opaque tin glaze. Decor: inglaze, square bosses and garland motif in black, grey-blue, turquoise, yellow. Upper edge = 7 cm	Boschetti-Maradi *et al*. (2004), cat. 64, fig. 18 (Lnr. 27056, Fnr. 46801-27)
Ofe 45	1443–1513? (1450–75)	Nidau, Hauptgasse 32, town hall, 1993	Fragment of a rectangular relief panel tile. Main motif: heraldic rose. Red body. White slip. Two-glaze technique: (1) heraldic rose petals: green transparent lead glaze; (2) rest of the tile: whitish opaque tin glaze. Decor: inglaze, blue lines and fillings. Height = 10.2 cm	Boschetti-Maradi *et al*. (2004), fig. 19 (Lnr. 27057, FZNr. 39871-6,3987-11)
Ofe 46	1443–1513? (1450–75)	Nidau, Hauptgasse 32, town hall, 1993	Fragment of a rectangular relief panel tile. Main motif: heraldic rose. Red body. Two-glaze technique: (1) heraldic rose petals: brown transparent lead glaze; (2) rest of the tile: whitish opaque tin glaze. Maximum length = 8.6 cm	Boschetti-Maradi *et al*. (2004), fig. 19 (Lnr. 27058. FZNr. 46804-5)
Ofe 47	1443–1513? (1450–75)	Nidau, Hauptgasse 32, town hall, 1993	Fragment of a rectangular relief panel tile. Main motif: not identifiable, probably heraldic rose. Red body. White opaque tin glaze. Decor: inglaze, blue lines and fillings. Left edge = 24 cm	Boschetti-Maradi *et al*. (2004), fig. 19 (Lnr. 27059, FZNr. 39887-4)
Ofe 52	1500–50	Bern, Minster platform, 1986	Fragment of a flat cornice corner tile. Red body. Beige slip. White, opaque tin glaze. Decor: inglaze, square bosses (grey-blue, black) and garland motif (black, grey-blue, turquoise). Lower edge = 15 cm	Roth Kaufmann *et al*. (1994), Plate 2 fig. 2.5, cat. 257 (Lnr. 27557, Fnr. 7512/234).
Ofe 69	End of 15th century	Bern, minster platform, 1986	Fragment of a flat, frame-less panel tile. Red body. Two-glaze technique. Ofe 69a: beige slip and white opaque tin glaze and inglaze decor (blue strikes), separated from Ofe 69b by a deep, black notch. Ofe 69b: white to reddish slip and green, transparent lead glaze. Height = 6.5 cm	Roth Kaufmann *et al*. (1994), cat. 256 (Lnr. 27575, Fnr. 7505-164)
Ofe 73	1450–1500?	Fraubrunnen, castle/ monastery, 1973	Two fragments of a flat panel tile with deep notches. Motif: continuous stylized crab pattern. Beige body. White slip. White opaque tin glaze. Decor: inglaze, blue fillings of the notches and blue strokes on the rim. Upper edge = 24 cm	Roth Kaufmann *et al.* (1994), similar to cat. 288 (Lnr. 27580, Fnr. 43119-1, small fragment: 43119-2)

Notes:

*The date according to stylistic arguments is shown in parentheses.

Fnr., Fund-Nummer; FZNr., Fundzettel-Nr.; Lnr., Laufend-Nr.

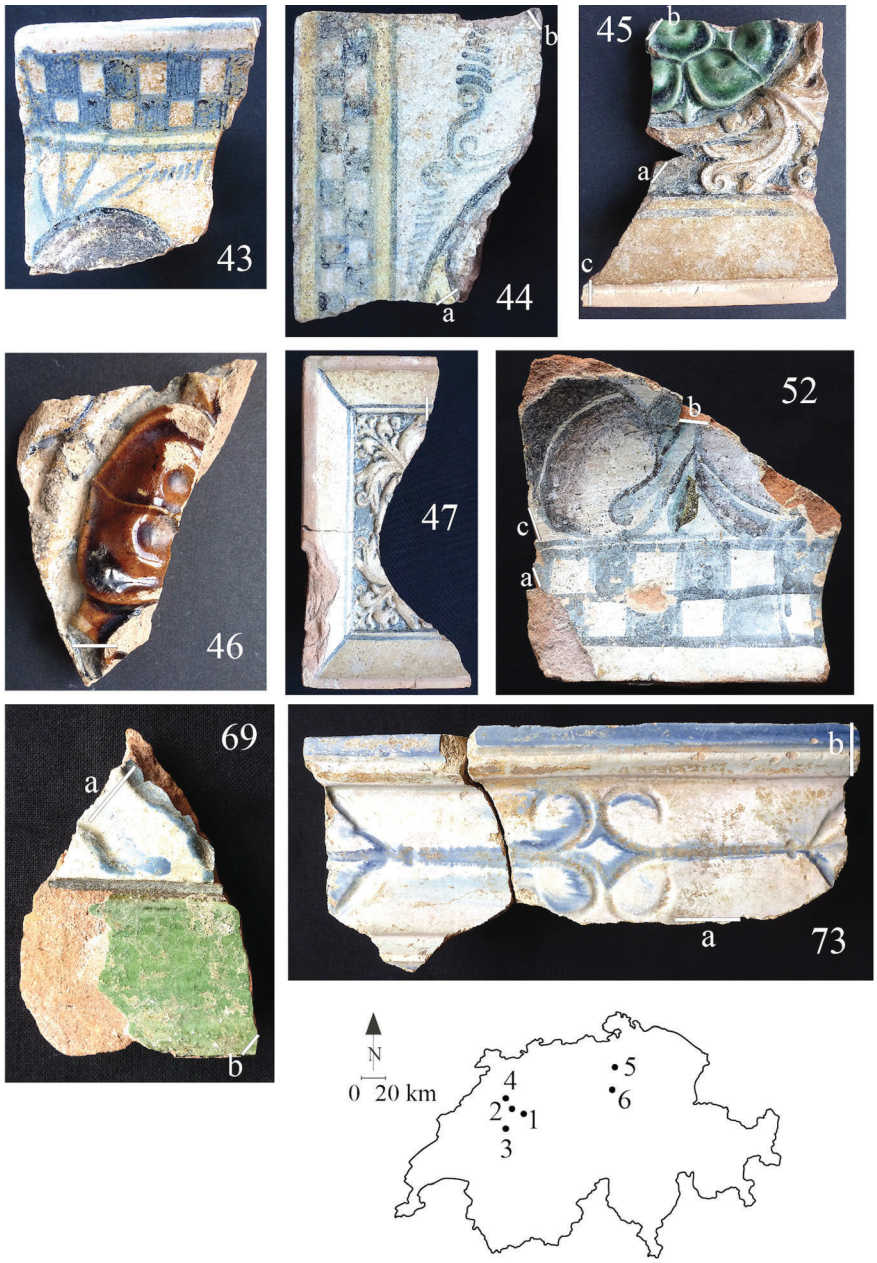

Figure 1 *Analysed objects, as described in Table 1. White bars = sections used for the scanning electron microscopy (SEM) analyses. Locations of the city sites in Switzerland: 1, Bern; 2, Fraubrunnen; 3, Fribourg; 4, Nidau; 5, Zürich; and 6, Zug.*

When polished, they were coated with an approximate 30 nm-thick carbon layer. Backscattered electron (BSE) images were collected with a scintillator-type detector out of these polished samples, using a Philips® FEI XL30 Sirion FEG scanning electron microscopy (SEM). Chemical

compositions were determined by energy-dispersive X-ray spectrometry (EDS), operated at a beam acceleration voltage at 20 kV, a beam current of 6.5 nA, 7.5 mm working distance and 50 s measuring time. Standardless quantification was performed using an SEM-EDS-ZAF (Z = atomic number, A = self-absorption effect, F = fluorescence effect) correction procedure of the intensities, using spot analyses (2 µm diameter), as well as larger area analyses of homogeneous areas. The detection limits for most oxides were about 0.2 wt%. The reliability of the results was checked measuring well-known glass standards (Corning C: PbO = 36.7 wt %, CoO = 0.17 wt%; DLH2: PbO = 35.0 wt%, CoO = 0.79 wt%). The relative mean deviation for major and minor oxide components was 2% for concentrations in the range of 20–100 wt%, 4% for 5–20 wt%, 10–20% for 1–5 wt% and $>$ 50% for $<$ 1 wt%.

RESULTS

All coloured paint strokes were opaque and lay on the tin-opacified white glaze with a sharp and wavy border, typical for the inglaze painting technique. Yellow was applied over the blue and the thin black lines over all other ceramic colours. The ceramic colours were all Si-Pb glasses.

Inglaze blue

Two major types of opaque blue were identified by SEM observations (Fig. 2, a, b). Blue I showed a heterogeneous distribution of small black and grey type A crystals in a glass matrix (Fig. 2, a, c). The former appeared as more or less perfect prismatic laths with a maximum length of 3.8 µm; the latter were more isometric with a maximum width of 1.8 µm. In contrast, blue II had no such grains (Fig. 2, b). The thicknesses of the paint strokes were markedly different: 50–120 µm for blue I and 100–240 µm for blue II. Another difference and further grouping were related to the cassiterite (SnO_2) content. Blue II contained a large number of these grains with dimensions up to 35 µm. Blue Ia showed usually a few small cassiterites that were probably mechanically taken over from the powdery, unfired white tin glaze underneath when the paint stroke was applied. On the other hand, Ofe 52 possessed a blue Ib with too many cassiterites for it to have been accidentally incorporated (Fig. 2, d). The variability of the cassiterite size and heterogeneity of the spatial distribution was characteristic for blue Ib and blue II. Both can therefore be classified as tin-opacified blue ceramic colours. Bulk and glass matrix analyses showed that cobalt is the chromophore for the blue hue, with much higher concentrations in blue I as in blue II (Table 2). All blues also had relatively high contents in Fe, Ni (apart from Ofe 44a) and, with the exception of Ofe 43 and Ofe 44b, Cu. Their concentrations were usually higher in blue I than in blue II. As expected from the microstructure, the SnO_2 content of blue I was lower as in blue II. The glass matrix of both blue showed variable concentrations of Fe, Co, Ni and Cu. These four elements could be related to the cobalt ore or the manufacturing of the blue as purposefully additions to alter the colour. The largest prismatic type A grains of blue I were a SiO_2 phase, probably cristobalite according to the crystal shape. The composition of the smaller black and grey type A grains such as shown in Figure 2c could only be approximated due to their small grain size. Compared with the glass matrix that surrounds them, they were richer in Na, Mg, Si, Sn, Ca, Fe, Co and Ni, with widely ranging proportions of these elements.

In addition to these crystals, few rounded to ellipsoidal grains (type B) with an intersertal-like internal texture were observed in the blue I of Ofe 46 (Fig. 2, e). They presented a Co- and Ni-richer, but Fe-poorer core and a Co- and Ni-poorer, but Fe-richer rim (Table 2). Similar cobalt pigments were reported in ninth-century Samarra blue glazes (Kleinmann 1991), which showed

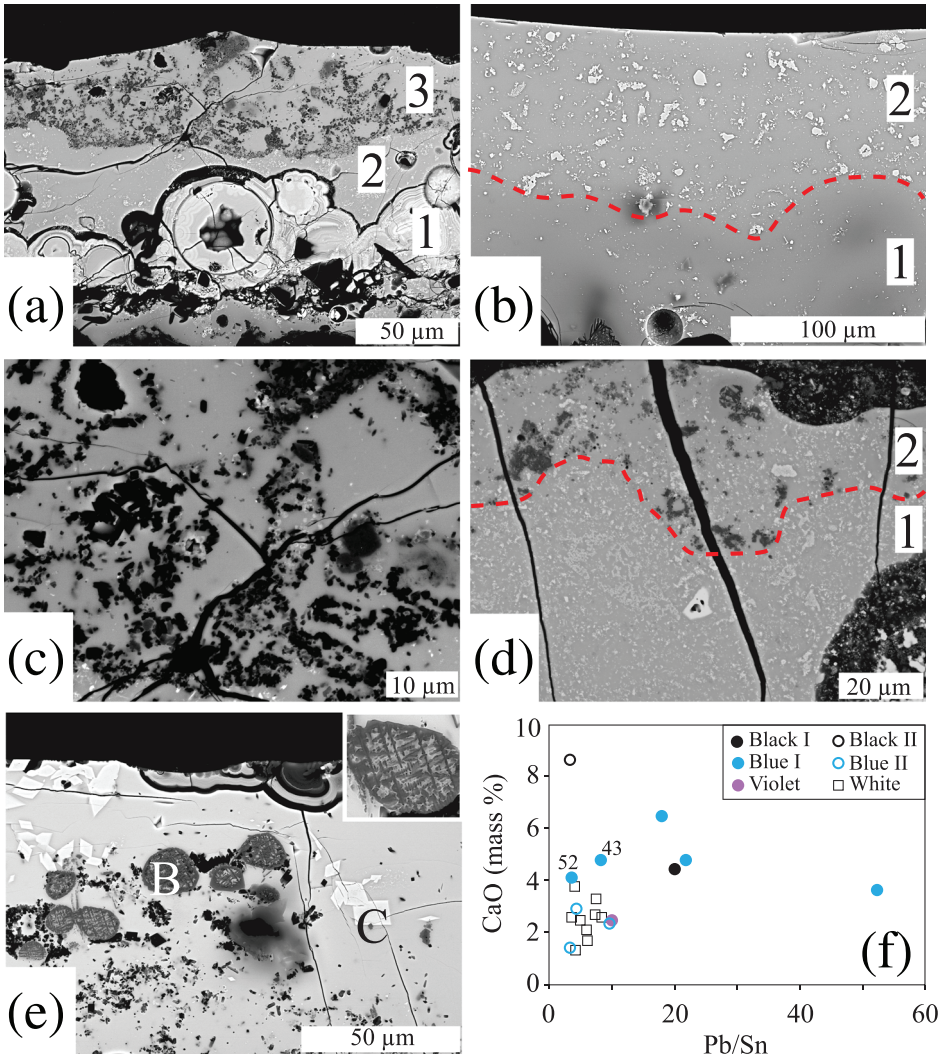

Figure 2 *Scanning electron microscopy-backscattered electron (SEM-BSE) images of sections showing the microstructure of the blue inglaze paintings. Dashed red lines = contacts. (a) Ofe 47: (1) severe degraded P-rich tin glaze; (2) uncontaminated tin glaze; and (3) blue Ia paint stroke with black to greyish colour pigments; (b) Ofe 73b: (1) tin glaze; and (2) blue II paint stroke with cassiterites (white grains); (c) enlarged view of the blue Ia paint stroke in (a: 3); (d) Ofe 52a: (1) tin glaze; and (2) blue Ib paint stroke with cassiterites and pigments; (e) Ofe 46: heterogeneous blue Ia; B = spherical to ellipsoidal safre grains with an internal intersertal texture; inlay = closer view of a 25 µm large ellipsoid; and C = large and undefined crystalline phases; and (f) distribution of the colours and tin-opacified glazes (Table 3) in the binary diagram CaO-Pb/Sn.*

large chemical variations due to the unlimited miscibility of di- and trivalent oxides for spinels with the general formula $(Co,Ni,Fe)(Co,Ni,Fe)_2O_4$. Ferrite spinels were identified by µ-Raman spectroscopy in cobalt blue glazes of 15th–16th-centuries Hispano-Moresque architectural tiles (Coentro *et al*. 2018). According to Kleinmann (1991), iron could have been present in the ore or the gangue, or was admixed during roasting (see below) to bind the sulfur.

Table 2 *Chemical composition of the colours determined by scanning electron microscopy (SEM) with energy-dispersive spectroscopy (SEM-EDS)*

An. no. (n)	*Maximum. thickness (µm)*	*Analysed surface (µm), spot*	*Na_2O*	*MgO*	*As_2O_3*	*Al_2O_3*	*SiO_2*	*Cl*	*K_2O*	*SnO_2*	*Sb_2O_3*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*	*CoO*	*NiO*	*CuO*	*PbO*
Opaque blue type I (bulk)																			
Ofe 43	98	120 × 50	1.4			2.0	44.0	0.2	2.4	4.9		4.5			2.2	1.8	2.0		34.6
Ofe 45a (3)	120	70 × 40	1.0			1.8	36.5		1.3	2.8		6.0			2.9	2.3	2.5	1.2	41.7
Ofe 46	95	100 × 50	1.1			1.5	30.0		0.9	1.2		3.4			3.5	2.1	1.6	1.3	53.3
Ofe 47 (2)	65	350 × 80	1.7			2.5	37.7		1.3	2.2		4.4			3.2	3.1	2.6	0.6	40.6
Ofe 52a (2)	50	50 × 15	1.3			1.7	34.7	0.2	0.6	12.9		4.0			1.4	1.0	1.3	0.5	40.4
Opaque blue type II (bulk)																			
Ofe 44a (3)	220	200 × 180	1.6			1.5	36.1		1.4	6.0		2.3			0.5	0.2		0.3	50.1
Ofe 44b	175	100 × 100	2.2			1.5	34.4	0.9	1.5	5.6		2.5			1.0	0.4	0.3		49.6
Ofe 69a (2)	240	400 × 300	2.5	0.5		1.9	38.8	0.5	0.9	10.0		2.8			2.3	0.7	0.4	0.5	38.2
Ofe 73b	100	350 × 80	2.2	0.3		2.6	39.7		0.8	12.9		1.4			0.7	0.6	0.4	0.2	38.2
Opaque blue type I (glass matrix)																			
Ofe 43		Spot	0.8			1.5	48.5	0.3	2.4	3.0		2.7			1.0	0.6	0.5		38.7
Ofe 45a (3)		Spot	1.0			2.7	34.9		1.6	1.3		0.7			2.4	1.1	0.3	1.6	52.3
Ofe 69a (3)		Spot	1.6	0.5		2.1	44.0		1.0	2.5		2.9			3.5	1.0	0.5	0.7	39.5
Opaque blue type II (glass matrix)																			
Ofe 73b (3)		Spot	1.6	0.4		4.0	46.9		1.1	1.2		1.1			0.8	0.6	0.4	0.3	41.5
Grain B																			
Ofe 46-P2c		10 × 8													21.9	32.0	46.1		
Ofe 46-P2r		Spot													55.1	22.3	22.6		

(*Continues*)

Table 2 *(Continued)*

An. no. (n)	*Maximum. thickness (μm)*	*Analysed surface (μm), spot*	*Na_2O*	*MgO*	*As_2O_3*	*Al_2O_3*	*SiO_2*	*Cl*	*K_2O*	*SnO_2*	*Sb_2O_3*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*	*CoO*	*NiO*	*CuO*	*PbO*
Grain C																			
Ofe 46 (5)		Spot					15.4			14.2					7.0	1.7	3.6		58.0
Opaque yellow (bulk)																			
Ofe 44a-18	70	80 × 20	1.1		0.3	2.1	39.1		1.6	4.1	9.7	2.3			1.2	0.4	0.3		37.8
Opaque yellow (glass matrix)																			
Ofe 44a-19		Spot	0.6			3.0	46.6		1.8	4.1		0.8			1.0	0.5	0.2		41.4
Pigment (Sn-Sb-Fe-Pb)																			
Ofe 44a-17		Spot								6.2	23.7				2.5				67.6
Ofe 44a-20		Spot								13.1	31.7				0.3				54.9
Opaque violet (bulk)																			
Ofe 44a	215	200 × 120	1.8				32.7	0.7	1.1	6.1		2.3		2.9	0.6				51.6
Opaque black type I (bulk)																			
Ofe 44a (2)	125	250 × 200	1.4			2.0	31.4		1.5	2.7		4.0		1.1	3.1	3.6	2.4	0.4	46.3
Opaque black type II (bulk)																			
Ofe 52b	245	300 × 80	0.2			1.8	27.6			13.1		7.8			1.4			9.0	39.1
Opaque black type I (glass matrix)																			
Ofe 44a (2)		Spot	1.6			2.2	33.2		1.4	1.9		1.5	0.2	1.3	1.3	1.3	0.3	0.5	53.3
Opaque black type II (glass matrix)																			
Ofe 52b (3)		Spot	0.5			3.2	30.7	0.2	0.3	1.5		3.7			1.5			7.2	51.2

(*Continues*)

Table 2 *(Continued)*

An. no. (n)	*Maximum. thickness (µm)*	*Analysed surface (µm), spot*	*Na_2O*	*MgO*	*As_2O_3*	*Al_2O_3*	*SiO_2*	*Cl*	*K_2O*	*SnO_2*	*Sb_2O_3*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*	*CoO*	*NiO*	*CuO*	*PbO*
Grain D1																			
Ofe 44a-12		Spot													2.5	54.1	42.1	1.3	
Ofe 44a-13		Spot													11.3	21.6	64.5	2.6	
Ofe 44a-15		10 × 8													15.2	38.6	44.0	2.2	
Ofe 44a-22		Spot												0.5	32.5	47.6	19.4		
Ofe 44a-23		Spot												0.6	18.0	64.7	16.7		
Ofe 44a-24		Spot												0.9	19.7	62.4	17.0		
Grain D2																			
Ofe 44a-35		Spot												1.3	0.9	7.1	89.5	1.2	
Ofe 44a-38		Spot												3.1	1.1	6.6	89.2		
Kentrolite																			
Ofe 44a (4)		50 × 50, spot					17.6			3.0		0.2		14.1	1.3	0.7	0.8		62.4
Cu pigment																			
Ofe 52b (2)		Spot													0.5			99.5	

Notes: The number of analyses for the mean is shown in parentheses.
Date are wt% normalized to 100.
Ofe 46-P2c and Ofe 46-P2r = core, respectively rim of the ellipsoidal pigment.

A third crystalline phase type C was present in Ofe 46, with mostly rhomboedric (maximum length 43 µm), and less prismatic shapes (Fig. 2, e). These thin crystals appeared white under the SEM and were rich in elongated inclusions of the surrounding glass and very tiny cassiterites. Their small thickness of maximum 0.18 µm hindered an exact chemical analysis. The results showed an Si-Sn-Fe-Co-Ni-Pb composition (Table 2). Unfortunately, the results of these chemical analyses did not allow any conclusion as to whether these grains were Fe-Co-Ni-olivines (Coentro *et al*. 2018).

Inglaze yellow

The yellow brushstroke reached a maximum thickness of 70 µm (Table 2). A multitude of heterogeneously distributed smallest crystallites (maximum diameter = 1.5 µm), which were brightly reflecting in the SEM-EDS image, lay in a glass matrix, along with (black) particles (SiO_2, probably cristobalite) and a few, larger cassiterites (Fig. 3, a, b).

These bright crystallites often have square cross-sections. They are Pb-Sn antimonates, as revealed by spot analyses, and are therefore the colouring pigments. By comparison, the matrix contained as colouring oxides mainly CoO and NiO (Table 2). The astonishing high level of Co in the yellow was not due to a voluntary addition, but to a diffusion from the blue below. This implied that the yellow crystals were previously embedded in an uncoloured glass. Like the tin glaze, the yellow colour was not very resistant to post-depositional changes (Fig. 3, a). The yellow was coated with a thin (25–50 µm thick), heavily weathered opaque white tin glaze that lowered the colour intensity and led to a matt yellow (Fig. 3, c).

Inglaze violet

This paint stroke had a maximum thickness of 215 µm. The SEM-BSE image showed a homogeneous distribution of the smallest individual cassiterites or cassiterite agglomerates (maximum diameter = 6 µm) in a glass matrix (Fig. 3, d). The SnO_2 content was around 6 wt% (Table 2). Since no Mn-rich crystals had been individuated, manganese (MgO 2.9 wt%) acted as a colouring oxide, dissolved in the glass matrix. Under the violet decoration, the white tin glaze had a slightly violet hue too, a visible Mn diffusion from the above paint layer during the glaze firing.

Inglaze black

There were two morphologically and chemically distinct types of black, which also differed by their stroke thickness: 125 µm for black I and 245 µm for black II. Figure 3 (e) reveals the heterogeneous structure of the former. Its glass matrix was full of tiny inclusions, morphologically and chemically very similar to the type A crystals of blue I (maximum size = 1 µm, black to greyish in the SEM-BSE image). However, these microcrystals contained no Sn compared with those of blue I, but instead Mn and a little Cu. In addition, there were larger Co- and Ni-bearing grains: (1) very rare irregularly shaped grains type B; (2) rounded to jagged shaped, homogeneous Fe-Co-Ni grains type D1, with or without Cu (Table 2); and (3) tiny rectangular Ni-Co grains type D2 with a jagged outline and maximum length of 6 µm (Fig. 3, g, and Table 2). Both were surrounded by a characteristic corona of very small square-shaped crystals, which had a Si-Ca-Mn-Fe-Co-Ni composition. Tiny euhedral cassiterites (maximum diameter = 1.5 µm) and square- to lance-shaped and thin Mn-rich crystals (light grey, maximum length = 48 µm) (Fig. 3, h, and Table 2) further represented crystalline phases. The chemical composition of the

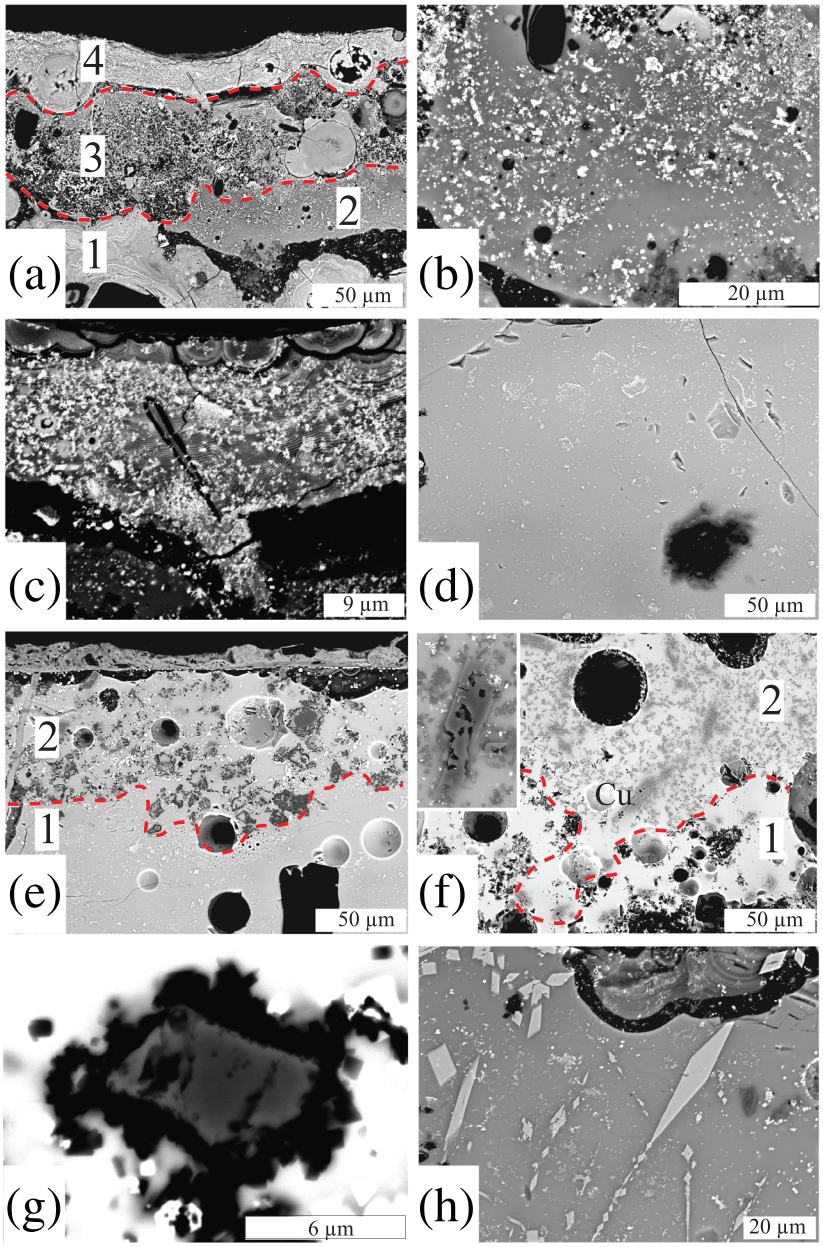

Figure 3 *Scanning electron microscopy-backscattered electron (SEM-BSE) images showing the microstructure of the yellow, violet and black inglaze paintings. Dashed red lines = contacts. (a) Ofe 44a: section through (1) the severe degraded P-rich tin glaze; (2) the fresh tin glaze; (3) the partly degraded yellow inglaze paint stroke; and (4) the outer tin glaze paint layer; (b) Ofe 44a: close-up of the yellow colour; (c) zoom in zone 4 of (3: a) showing a severe alteration of this outer layer with many tiny cassiterite crystals; (d) Ofe 44a: section through the homogeneous violet with few cassiterites; (e) Ofe 44a: section through (1) the tin glaze; and (2) the black I inglaze paint stroke, rich in grey and black particles, with a heavily degraded surface; (f) Ofe 52b: section through (1) the contact zone of the tin glaze; and (2) the black II inglaze paint stroke, rich in copper particles (grey); inlay = 22 µm-long skeletal copper crystal; (g) Ofe 44a: black I, Ni-Co grain D2; and (h) Ofe 44a: lanceolate-shaped kentrolite crystals in black I.*

latter came very close to that of kentrolite $Pb_2Mn_2^{3+}Si_2O_9$, if one takes into account that for such thin crystals the electron beam has certainly also analysed parts of the glass matrix underneath. The bulk and the glass matrix of black I were found to contain high concentrations of Mn, Fe, Co, Ni and Cu (Table 2).

Black II showed a homogeneous distribution of the smallest, partly agglomerated cassiterites (agglomerates: maximum size = 4.2 µm), together with a multitude of small euhedral prisms (maximum length = 3.2 µm) and few large, skeletal crystals with a maximal length of 22 µm (both grey in the SEM-BSE image) in the glass matrix (Fig. 3, f). These crystals were intergrown with isometric cassiterites. Needle-like SiO_2 crystals (cristobalite?) were rare. The grey crystals were pure CuO, as evidenced by spot analyses (Table 2). Accordingly, the CuO values of the bulk and the matrix were high, while the SnO_2 content of the bulk and the glass matrix lay in the range of the white tin glazes.

DISCUSSION

Inglaze blue

The impact of the cobalt concentration in a glaze is well known (Rhodes 1973). In a ceramic colour, 0.2 wt% CoO produce a medium blue, 0.5 wt% a strong blue, 1 wt% a very dark blue and $>$ 1 wt% a dense blue-black or black. Evidently, the colour of blue I derives from its high Co content, which is further darkened by the multitude of crystals in it. On the other hand, Ni in conjunction with Co gives a deep blue or black, which could correspond to Piccolpasso's '*zaffera nera*' (Agosti *et al*. 1997; Bandini *et al*. 1997). The lower Co content, in connection with the numerous cassiterites, results in blue II. To cover the white tin glaze, blue I could therefore be applied in a thinner layer than blue II.

Blue ceramic colours with a Co-Cu-Fe-Ni (Mn) source signature were described from the 14th to the beginning 16th centuries tin-glazed objects in Spain (Roldán *et al*. 2006; Pérez-Arentegui *et al*. 2009; Coentro *et al*. 2014, 2018) and Italy (Zucchiatti *et al*. 2006). Similar Co-Fe-Ni grains as type B were found in della Robbia blues before 1520 (Zucchiatti and Bouquillon 2011). For the studied objects, copper could rarely be found in the spinels type B or D. Since this element is enriched in the glass matrix compared with the bulk, it might have been intentionally introduced during the synthesis of the blue, or accidentally added during pigment processing such as grinding in a brass mortar (Matin and Pollard 2017). The absence of As also fits in with the observation that this element was only detected in blue ceramic colours from 1517 onwards (Zucchiatti *et al*. 2006). Zn was found in Florentine 14th-century enamels, but not in mid-15th and late 15th-century ones, contrasting with the presence of Ni in the latter, but not in the former (Verità *et al*. 2013). The changes of impurities in 15th-century Venetian blue glass indicate German ore sources (Verità 2007). It is a common belief that at the end of the 15th century the cobalt originates from Germany (Saxony, 'Erzgebirge'). Skutterudite $(Co,Fe,Ni)As_{2-3}$ is there the most important cobalt ore, with variable amounts of Fe, Co and Ni (Förster 2018). The ores were calcined, respectively oxidized, to safre (Minerophilus Freibergensis 1730, Horschik 1979, Hammer 2004), consisting of spinels with an expected wide variability in their Fe-Co-Ni composition.

According to Kunckel (1679) and Minerophilus Freibergensis (1730), the safre was transformed into a blue glass named smalt by milling, mixing with quartz and a K-flux (potash or K-tartar), or a K-flux and salt, and melting. In the technical literature of the time, both terms (safre, smalt) were unfortunately used synonymously. To make matters worse, the smalt does not necessarily have to be a blue, pure K-glass. In addition to K, Pb (metallic Pb, Pb oxide or

sulfide) or just Pb alone can also have been mixed as a flux with the sand, as inferred from chemical analyses (Gratuze *et al*. 1996; Zucchiatti *et al*. 2006). CaO could have been present in the original ore as calcite intergrowth or was added as a supplementary flux. The mixture was calcined and melted. If the temperatures were low, an opaque deep blue frit was obtained, consisting of many pigments (spinels) and some blue glass. If the temperatures were high enough, the whole mixture could be melted, which then turned into a blue, transparent, inclusion-free glass granulate, when quenched. Both were milled in a next step.

As far as the examined Co-bearing blue I and black I are concerned, it is very likely that the spinel grains of type B and D represent relict fragments of the original safre. While the angular grain shapes are due to grinding, the rounded to jagged outlines could indicate dissolution processes during the manufacture of the blue glass. This is further supported by the corona microstructure around these safre relicts, which probably indicate that the latter were being absorbed by the surrounding melt during prograde heating, and that the tiny corona phases crystallized out of this contact melt when the coloured glass cooled. The intersertal texture of pigment B is more difficult to explain – is the matrix really glassy? Can this texture be explained by crystallization during rapid cooling (quenching) of a liquid, obtained by over firing former Fe-Co-Ni arsenides or sulfides? The matrix glasses in blue I, blue II and black I have far too little K to be called smalt. Their flux was a Pb phase, as evidenced by the chemical compositions.

Blue Ia is interpreted as the case where a blue frit powder was used as blue ceramic colour, blue Ib as the mix of such powder with ground tin glaze, while blue II could correspond to a blend of ground blue glass with tin glaze. This hypothesis is supported by the Pb/Sn ratios of blue II and blue I of Ofe 52, which are, in contrast to the majority of blue I, in the same range as the tin glazes (Table 3 and Fig. 2, f). The idiomorphic outlines of crystals C show, as those of A, that they must have been in equilibrium with the enveloping blue melt during the glaze (and inglaze colour) firing. They will therefore represent pro- to retrograde crystallization steps from such melts.

The CaO content too shows that both blues originate from different recipes or from different sources. Indeed, blue I is much richer in CaO than blue II, which corresponds to that of the tin glazes (Fig. 2, f).

Inglaze yellow

Three artificial yellow pigments can be found as glass and ceramic colour and opacifier: $Pb_2Sb_2O_7$ ('Naples Yellow'), $PbSnO_3$ and $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$. The use of Pb antimonate dates to the 18th dynasty (1570–1292 BCE) in Egypt (Kacmarczyk and Hedges 1983), whereas Pb stannate was made only from the second century BCE onwards (Tite *et al*. 2008). Pb-Sn antimonate is a rare pigment and has been found thus far in a few 14th–19th centuries Italian (Sandalinas *et al*. 2006; Duran *et al*. 2011; Chiarantini *et al*. 2015; Seccaroni 2016), Portuguese (Coentro *et al*. 2012) and 18th-century French (Maggetti *et al*. 2009) tin-glazed ceramics. The studied yellow pertains therefore to the oldest examples of this ceramic pigment type reported so far. It cannot be deduced from the microstructure and the SEM-EDS results whether the yellow crystals were produced in a single high-temperature synthesis step or by the 'anime' technique, in which previously synthesized and milled yellow crystals are added directly into a low-temperature translucent glass melt (Moretti and Hreglich 1984, 2005). According to Dik *et al*. (2005), Pb antimonate pigments were absent for about a millennium in the Western world and reintroduced only at the end of the 15th century, probably through Byzantine glass and ceramic immigrants to Venetian glass-making shops after the Islamic conquest of Damascus (beginning of the 15th century) and

Table 3 *Recalculated composition (wt% normalized to 100) of the colour paints subtracting all chromophores and fixing Fe_2O_3 to the value of the related tin glaze. The composition of the tin glazes was according to Maggetti (2020). The latter were not recalculated in order to show the contaminations from the overlying paints. The number of analyses for the mean is shown in parentheses.*

An. no. (n)		*Na_2O*	*MgO*	*Al_2O_3*	*SiO_2*	*Cl*	*K_2O*	*SnO_2*	*CaO*	*TiO_2*	*Fe_2O_3*	*CoO*	*NiO*	*CuO*	*PbO*	*Pb/Sn*
Ofe 43 (3)	Tin glaze	1.5		1.5	41.1	0.5	1.8	6.7	3.3		0.7				42.9	7.5
	Blue I	1.5		2.1	46.5	0.2	2.5	5.2	4.8		0.7				36.5	8.3
Ofe 44a	Tin glaze	2.2		1.5	37.1	1.0	1.3	6.6	2.6		0.5				47.2	8.4
	Blue II	1.6		1.5	36.3		1.4	6.0	2.3		0.5				50.4	9.9
	Violet	1.9			33.8	0.7	1.1	6.3	2.4		0.5				53.3	10.0
	Black I	1.6		2.2	34.9		1.7	3.0	4.4	0.1	0.6				51.5	20.2
Ofe 45c (2)	Tin glaze	1.7		1.2	34.1	0.7	1.0	7.8	2.7		0.6				50.2	7.6
	Blue I	1.1		3.0	39.4		1.4	3.0	6.5		0.6				45.0	17.7
Ofe 46a	Tin glaze	1.2		1.0	40.4	0.5	1.0	8.4	1.7		0.5			1.0	44.3	6.2
	Blue I	1.2		1.6	32.7	0.1	1.0	1.3	3.7		0.5				57.9	52.5
Ofe 47	Tin glaze	1.7		1.0	37.1	0.4	0.6	9.2	2.1		0.5			0.2	47.2	6.0
	Blue I	1.9		2.7	41.5	0.1	1.4	2.4	4.8		0.5				44.7	22.0
Ofe 52a	Tin glaze	1.2			30.4	0.5	0.6	11.8	2.5		1.0	0.5	0.4	0.5	50.6	5.1
	Blue I	1.3		1.8	35.9	0.2	0.6	13.3	4.1		1.0				41.8	3.7
Ofe 52b (2)	Tin glaze	1.4		1.0	33.6	0.1	0.3	14.7	2.6		0.6			0.5	45.2	3.6
	Black II	0.2		2.0	30.6			14.5	8.6		0.7				43.3	3.5
Ofe 69a	Tin glaze	2.2	0.7	2.2	42.2		1.3	10.6	3.8		1.0			0.2	35.8	4.0
	Blue II	2.6	0.5	2.0	40.0	0.5	0.9	10.3	2.9		1.0				39.3	4.5
Ofe 73	Tin glaze	1.7	0.4	1.9	35.5		0.7	12.5	1.3		0.4				45.6	4.3
	Blue II	2.2	0.3	2.6	40.4		0.8	13.1	1.4		0.4				38.8	3.5

Constantinople (1452). Many recipes on how to synthesize ceramic yellows can be found in manuscripts such as the 'Calabranci code' (Berti 2003; Chiarantini *et al*. 2015), Piccolpasso (1557–58) or in treatises such as Biringuccio (1540).

Inglaze violet

The violet colour is chemically and microstructurally very similar to the underlying tin-opacified white glaze. Effectively subtracting the Mn concentration of the violet, an overall composition close to the tin glaze results (Table 3). This accordance is further documented in the matching Pb/Sn ratio (Fig. 2, f). Similar Mn violets were found in Italian Renaissance ceramics (Chapoulie *et al*. 2005; Higgott *et al*. 2007).

Inglaze black

Black I is, apart from its MnO concentration, microstructurally, chemically and, in terms of colour pigments, very similar to blue I. Its Pb/Sn ratio is in the range of blue I (Table 3 and Fig. 2, f). It is therefore very likely that a small amount of an Mn pigment was added to a blue I recipe to achieve the deep black hue. No relict of such an original addition could be found. Kentrolite was identified in Mn browns of Islamic (Molera *et al*. 2013) and Hispano-Moresque glazes (Coentro *et al*. 2018). Their lanceolate grain shape is typical of rapid precipitation from a melt, which suggests that it occurred as a retrograde crystallization during the cooling phase of the glost firing. This fits well with kentrolite's stability field of approximately 650–840°C (Molera *et al*. 2013).

As for black II, Cu-black glazes develop very quickly if one adds more CuO to a glaze than it can dissolve (Matthes 1990). In this case, copious amounts of Cu were added to a tin glaze, which is reflected in its similar Pb/Sn ratio (Table 3 and Fig. 2, f). But this tin glaze was made according to a different recipe, because its CaO concentration (8.6 wt%) is, in comparison with the others, twice as high. Visibly, both blacks are different from the usual Fe-Mn-black of Iberian 10th–12th centuries pottery (Coentro *et al*. 2012) or Italian Renaissance majolica (Zucchiatti *et al*. 2000; Higgott *et al*. 2007).

CONCLUSIONS

The studied samples pertained to the first inglaze ceramic colours realised on tin-glazed stove tiles from Switzerland. The blue, yellow, violet and black colours were silica- and Pb-rich glasses, opacified by submillimetre crystallites suspended in the glass matrix. The colouring was caused by (1) ions dissolved in the matrix, (2) crystalline inclusions or (3) a combination of both. The analyses showed that the Bernese potters used two types of ceramic paints, produced following two major techniques. The almost cassiterite-free first type included: (1) a Co blue I with relic 'safre' Fe-Co-Ni spinels; (2) a yellow full of Pb-Sb-Sn particles; and (3) a black I obtained by admixing a small amount of MnO to the blue I. The detection of a Pb-Sn-Sb yellow pigment is a significant addition to previously reported occurrences of this rare ceramic pigment in the studied time span. The second ceramic paint type was achieved by adding Fe-Co-Ni- (resulting in blue II), Mn- (violet) or Cu- (black II) rich glass powders to already prepared tin-opacified white glaze powders. As the very low K content of the blue matrix glass showed, the blue (and black I) colour could not have been produced according to the traditional smalt recipe. In this different recipe, a Pb flux was used. Due to the CaO content, at least two tin glaze recipes could be distinguished. The colour palette of these mid-15th–early 16th centuries

stove tiles is, with the exception of the blacks, in good agreement with conventional pigments of this period. The question arises whether the ceramic colours were the result of local experimentation or if they were sourced from abroad. It is hard to imagine that local potters could have mastered such complex colour syntheses considering the problems they had with the introduction of the new tin glaze technique (Maggetti 2020). This is supported by the yellow pigment, which does not correspond to the then common and widespread Pb antimonate ('Naples Yellow'), but to the very rare triple Pb-Sb-Sn oxide. In comparison with contemporaneous Italian or Spanish pottery, the colours were applied very discreetly, a further sign that the potters first had to familiarize themselves with the new ceramic colours, which in turn speaks of the purchase of already prepared colours.

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