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A first approach to reconstruct the production technology of Zsolnay ceramic panel paintings with oil painting effect

Bernadett Bajnóczi [a,*], Máté Szabó [a], Zoltán May [b], Péter Rostás [c], Mária Tóth [a]

[a] Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Eötvös Loránd Research Network (ELKH), H-1112 Budapest, Budaörsi út 45, Hungary
[b] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Eötvös Loránd Research Network (ELKH), H-1117 Magyar tudósok körútja 2, Budapest, Hungary
[c] Kiscell Museum of the Budapest History Museum, H-1037 Budapest, Kiscelli utca 108, Hungary

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ABSTRACT

Colourful and artistic ceramic panel paintings that realistically imitate oil paintings were one of the innovations of the Hungarian Zsolnay ceramic factory. Ten large ceramic panel paintings and two overdoor compositions (each containing three panels) decorated the Saint Stephen Hall in the palace of the Buda Castle (Budapest) established around the turn of the 19th and 20th centuries. However, the ceramic paintings were destroyed during World War II. In this study, three experimental Zsolnay panel paintings, as preparatory pieces for the original series, were examined to reconstruct the material usage and the production technology. Microanalytical investigation of the samples detached from one of the experimental panel paintings (portrait of King Béla IV) demonstrated that the panel, made of porous ceramic known as pyrogranite, was first covered by a white clay slip layer, and then by a primary white tin glaze layer, which served as a "ground" for the painting. The portrait of King Béla IV and the surrounding golden decorative motifs were created with different technologies. Coloured clay pastes (slips) were used to paint the portrait, which was then covered by a secondary transparent lead glaze, whereas a blue glaze covered by a thin layer of gold paint was applied over the primary glaze of the golden motifs. Non-destructive handheld XRF analysis revealed slight differences between the three experimental panel paintings, particularly in the tin content of the primary glaze layer and the colourants used, which were possibly related to the experimentation performed at the Zsolnay factory before the creation of the final paintings.

1. Introduction

The Zsolnay ceramic factory was established in Pécs (Hungary) in 1853 and initially produced clay pipes, bricks, architectural terracotta elements and other ceramic products, such as dishes. Vilmos Zsolnay became the factory director from 1865. He propelled the factory to global recognition by showcasing its innovative ceramics made to high technological and artistic standards at world fairs and international exhibitions, including the 1873 World Fair in Vienna (Austria), and at the 1878 World Fair in Paris (France) (Rúzsás, 1954; Pataky, 1962; Mattyasovszky Zsolnay and Hárs, 1971; Hárs, 1988). Vilmos Zsolnay was regarded by his contemporaries as "the greatest Hungarian potter".

In the middle and second half of the 19th century, the period of Historicism saw leading European ceramists, such as Théodore Deck and Clement Massier in France, Hermann August Seger in Berlin and the Mintons in England, revive historical forms, pottery production technologies and firing processes (Mundt, 2002). Similarly, Vilmos Zsolnay and his co-workers, including family members, were also interested in and inspired by, either technologically or stylistically, the decorated pottery productions of past centuries, such as the Italian Renaissance lustred and *istoriato* maiolica, the French Renaissance tableware of Bernard Palissy, the Ottoman-Iznik pottery and the oriental (Chinese, Japanese) ceramics (Pataky, 1962; Mattyasovszky Zsolnay and Hárs, 1971; Hárs, 1988). Archaeological artefacts and folk art pottery were sources of inspiration as well. To improve old technologies and develop new products, Vilmos Zsolnay conducted numerous experiments using several kinds of clays and glazes. He cooperated with renowned Hungarian chemists, like Vince Wartha and Lajos Petrik.

The factory produced artistic pottery for decorative purpose (e.g., Csenkey, 2000; Csenkey et al., 2017) and ceramics for personal use, as

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* Corresponding author.
E-mail address: bajnoczi.bernadett@csfk.org (B. Bajnóczi).

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Fig. 1. Zsolnay ceramic panel paintings analysed in this study (from left to right): portraits of King Béla IV, King Endre III and Saint Imre.

well as architectural and industrial ceramics. The primary innovations of the Zsolnay factory were the development of the following high-quality ceramic products[1]:

i) Porcelain-faience, a porous stoneware, whose ceramic paste was composed of kaolin, white clay, quartz sand and feldspar. Vilmos Zsolnay developed a new soft porcelain (feldspathic) glaze of ivory colour and a high-temperature novel plastic decoration technique (overglaze painting, "émail"). Porcelain-faience was produced from the mid-1870s and was used for decorative ceramics and table services (Pataky, 1962; Mattyasovszky Zsolnay and Hárs, 1971; Hárs, 1988). The unique porcelain-faience products received a Grand Prix at the 1878 World Fair in Paris, and Vilmos Zsolnay was awarded the French Legion of Honour.

ii) Eosin, a multi-coloured, iridescent metallic lustre glaze, which later became overglaze painting, that was prepared by reducing firing (Pataky, 1962; Hárs, 1963; Caiger-Smith, 1985; Csenkey, 2000). The term derives from *Eos*, the Greek goddess of dawn, referring to the light red iridescence of the first prepared hue, although, several other hues (e.g., blue, green, purple) were later created. Eosin glazing was developed in the early 1890s by Vilmos Zsolnay, and eosin products were first made in 1893 (Pataky, 1962; Mattyasovszky Zsolnay and Hárs, 1971; Hárs, 1963, 1988). Lustre ware became Zsolnay's most unique and inimitable product, and eosin was applied to decorative objects (mainly Art Nouveau and Art Deco style) and building ornaments.

iii) Pyrogranite, a series of ceramic products developed by Zsolnay in the 1880s and widely used from the early 1890s (Nikelszky, 1959; Pataky, 1962). The trade name combines the words 'pyro', which refers to the high temperature at which the products are burnt, and 'granite', which signifies durability (hardness). Due to its frost- and acid-resistance qualities, pyrogranite was used primarily for architectural features, such as roof tiles, as well as indoor and outdoor decorative ceramics (Hajtó, 2016). Pyrogranite was produced in unglazed and glazed (maiolica-glazed, i.e., coloured tin-glazed or eosin-glazed) versions. The most famous Hungarian architects used glazed and non-glazed pyrogranite ceramics on their public and private buildings, typically built in the Art Nouveau (Secession) style, that were erected in the territory of the Austro-Hungarian Monarchy and the surrounding Central European countries during the late 19th and early 20th centuries (Mattyasovszky-Zsolnay, 1954; Mattyasovszky-Zsolnay et al., 2005; Vízy, 2011; Merényi, 2015).

In addition to the high-quality ceramic products that are well-known today, other technological innovations were also elaborated on by Vilmos Zsolnay. Vince Wartha (1908) stated that the French ceramist Théodore Deck was the first to produce large ceramic products that imitated paintings. Deck collaborated with the Swiss painter Albert Anker and produced c. 500 faience wall plates and wall panels from the mid-1860s to the early 1890s (Kuthy, 1985). The precursor to faience painting (the coloured modern majolica technique) was the Italian Renaissance *istoriato* maiolica (cf. Liverani, 1960; Caiger-Smith, 1973). Likely motivated by this successful collaboration, Vilmos Zsolnay began to produce artistic ceramic paintings, as well[2]. Wartha (1908) wrote that for the ceramic paintings, Théodore Deck used metal oxides mixed with glaze, which he applied to a raw faience base and then covered it with a low-temperature glaze. Zsolnay improved the production of ceramic paintings with a lead-free, feldspathic glaze, thus making them more durable (Wartha, 1908). This method probably led to the colourful "majolica" wall plates and the decorative plates and vases produced by Zsolnay from the early 1880s, which were richly coloured and comprised of complex, painting-like imagery, stylistically similar to Italian *istoriato* maiolica. However, for these ceramics, Zsolnay actually made a porcelain-faience body that was covered with a feldspathic glaze and a high-temperature "émail" (Csenkey et al., 2017).

After several years of experimentation in the 1870–80s, Zsolnay exhibited ceramic paintings fired on red terracotta panels at the National Exhibition in Budapest in 1885 (Zsolnay and M. Zsolnay, 1980). These ceramic panels were specifically developed for fine art purposes using

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[1] http://www.zsolnay.hu

[2] https://collections.imm.hu/gyujtemeny/keramiakep/12921?npn=1

ceramic surfaces as “canvas”. The first pieces were characterised by sketchiness and the scant use of colours. Later, however, with improvements in panel painting techniques, they became more colourful and more richly pigmented, and they realistically imitated oil paintings (Mattyasovszky Zsolnay and Hárs, 1971). The artistic panel paintings, prepared by educated painters or sometimes by Vilmos Zsolnay, were reproduction or original artworks that depicted landscapes, portraits or genre paintings (Zsolnay and M. Zsolnay, 1980). Contemporaneous descriptions about the production technology of the ceramic panel paintings by Wartha (1892, 1905) revealed that clay pastes (slips, i.e., slurries of fine-grained clay suspended in water) mixed with metal oxides were applied over the (raw or already-fired) clay panel, which were then covered with a glaze and fired. This technique is difficult, because during creation the painter cannot see the colours, but must read them from a numbered table, as the greyish green or blue pastes used for painting obtained their true colour only after firing, when the glaze impregnates the pastes and makes them luminous (Zsolnay and M. Zsolnay, 1980; Mattyasovszky Zsolnay and Hárs, 1971). Unglazed ceramic panel paintings imitated frescoes (Zsolnay and M. Zsolnay, 1980; Mattyasovszky Zsolnay and Hárs, 1971). Later pyrogranite panels were used for the paintings, as well.

Although artistic ceramic panel paintings were considered suitable inner and outer building decorations, Zsolnay and M. Zsolnay (1980) state that they were only used in the territory of Hungary once, in the Saint Stephen Hall in the palace of the Buda Castle (Budapest). The series was composed of ten large ceramic panel paintings that depicted the portraits of the kings and saints of the Hungarian Árpád dynasty and two overdoor compositions (each containing three panels) that illustrated the coronation of King Stephen, and the scene “King Stephen and Bishop Saint Gerhard evangelize the people”, which decorated the Saint Stephen Hall established around the turn of the 19th and 20th centuries (Rostás, 2001, 2009). Pyrogranite panels were used for the ceramic paintings (Nikelszky, 1959), and the oil painting models were designed by the Hungarian painter Ignác Roskovics (Rostás, 2009). Unfortunately, these ceramic panel paintings were destroyed during World War II. Reconstruction of the Saint Stephen Hall was recently begun, involving the reproduction of the room’s interior and decorations, including the ceramic panel paintings. The preserved experimental paintings made by the Zsolnay factory, as preparatory pieces for the original series before the creation of the final products, may help to determine the materials and production technology used. To support the development of the production technology of the replica paintings, the present study aims to examine the materials (pyrogranite ceramic panel, glazes and colourants) of three preserved experimental panel paintings, including the portrait of King Béla IV in detail (Fig. 1).

2. Materials and methods

Digital microscopy and non-destructive handheld X-ray fluorescence analyses were performed preliminarily on the surface of three preserved panel paintings: the portraits of King Endre III (h: 55.5 cm, w: 46 cm, exhibited at the Budapest History Museum), King Béla IV (h: 157.1 cm, w: 68.6 cm) and Saint Imre (h: 157 cm, w: 68.3 cm) (Fig. 1). Applied equipment: Dino-Lite AM4113T-FVW digital UV/VIS LED USB microscope and SPECTRO xSORT Combi handheld XRF spectrometer (parameters: Peltier cooling, Rh anode X-ray tube, energy-dispersive SDD detector, 15–50 kV, 30–120 μA, ‘Light Elements’ calibration, 3 mm measurement area, 60 sec acquisition time, evaluation of spectra using Spectro XRF Analyzer Pro 2.2.2 software).

Due to the high artistic and historic value of the experimental paintings, only limited sampling of two ceramic paintings, the portraits of King Béla IV and Saint Imre (Fig. 1), was allowed. Small-sized samples were carefully detached at the damaged outer rims of the glazed ceramic panel of the King Béla IV portrait, the intact parts of the portrait were not sampled. The yellowish pyrogranite body was sampled from the back side of the ceramic panel (*sample 1*), and the glaze, together with the body, was sampled from the front side: at the light blue, red and yellow areas of the portrait, i.e., the clothing (*samples 3, 4 and 5*), and at the surrounding golden decorative motifs (*sample 2*). Brush strokes are clearly visible in the coloured areas of the portrait, whereas none are seen in the area of the golden decorative motifs. Instead, the golden motifs are underlaid with a blue layer, and a white glaze that covers the entire front surface of the ceramic panel is visible below it. For the panel of Saint Imre portrait, only the whitish body that contains greyish glaze patches was sampled from the back side of the ceramic panel; no other sampling was permitted. The King Endre III portrait was analysed only by handheld XRF due to sampling restrictions.

The phase composition of the pyrogranite ceramic bodies was determined by X-ray diffraction (XRD) analysis using a RIGAKU MINIFLEX 600 diffractometer with Bragg-Brentano alignment (instrumental parameters: CuKα radiation, 40 kV tension, 15 mA intensity, $0.05^\circ 2\Theta$ step size, 1° detector slit, 1° divergence slit, graphite monochromator).

Polished and carbon-coated cross sections were prepared perpendicular to the glaze-body interface of the samples to study the sequence and composition of the applied layers, as well as the colourants. For the microtextural and microchemical analysis a JEOL Superprobe-733 electron microprobe, equipped with an Oxford Instruments AZtec X-ACT Premium SDD type energy-dispersive X-ray spectrometer (EDX), was used (operating conditions: 20 kV acceleration voltage, 6nA beam current). For the chemical analysis of the glazes, well-known artificial glasses (NMNH 117218–4, −1, −2, −3, i.e., Corning archaeological reference glasses A, B, C and D; Adlington, 2017), provided by the Department of Mineral Sciences, Smithsonian Institution (USA) were used as reference materials for the main elements, copper and barium, whereas SnO_2 was used for tin, pure metal for cobalt, and Zn_2SiO_4 for Zn (provided by the Taylor Co, Stanford, California, USA). The ‘bulk’ chemical composition of the primary glaze was determined with area measurements including the tin oxide opacifier and other characteristic inclusions. Areas up to 120 × 60 μm (*samples 3, 4 and 5*) and 150 × 30 μm (*sample 2*) were measured in the primary glaze of the King Béla IV painting, and areas up to 450 × 350 μm were analysed in the primary glaze of the Saint Imre painting (100 s acquisition time, at least three measurements per sample). The vitreous matrix of the glaze layers was analysed using spot measurements (1 μm, 40 s acquisition time). Area and spot measurements, varying between 98 and 102 wt% oxide totals, were averaged. Spot measurements (40 s acquisition time) were also performed on the inclusions, pigments and newly formed crystals in the glazes, as well as on the components of the ceramic body; the references were natural and artificial materials provided by the Taylor Co. (Stanford, California, USA). X-ray maps showing the distribution of elements in the applied layers were acquired in 30 min.

Phase identification of the crystalline compounds in the blue glaze (*samples 2*), in the white slip layer beneath the primary white glaze and in the light blue slip paint layer covering the white glaze (*sample 3*) was performed on polished cross sections using a RIGAKU D/MAX RAPID II micro-X-ray diffractometer. This X-ray diffraction system is equipped with a curved image plate detector, a sealed tubed X-ray generator and a microfocus type MM003, and was designed specifically for micro-area analyses. Phase identification on this system occurs at high spatial resolution, using collimators ranging from 800 to 10 μms. The system with Cu Kα source operates at 50 keV and 0.6 mA. A built-in CCD camera is used to select the area of analysis. A laser scanning readout system reads the imaging plate detector in approx. 1 min. RIGAKU 2DP software is used to record the diffraction image from the laser readout. For each XRD pattern, the interpretable 2Θ region is selected manually. RIGAKU PDXL 1.8 integrated X-ray powder diffraction software is used for data processing. The following analytical conditions were used: 30 and 100 μm collimators, 10–30-120 min measurement time, ω (horizontal rotation) axis = 20–25, ϕ (tilt) axis = 15–25. Limitations of the micro-XRD analysis regarding data processing and evaluation are discussed by Mozgai et al. (2019).

The chemical composition (major and minor elements) of the

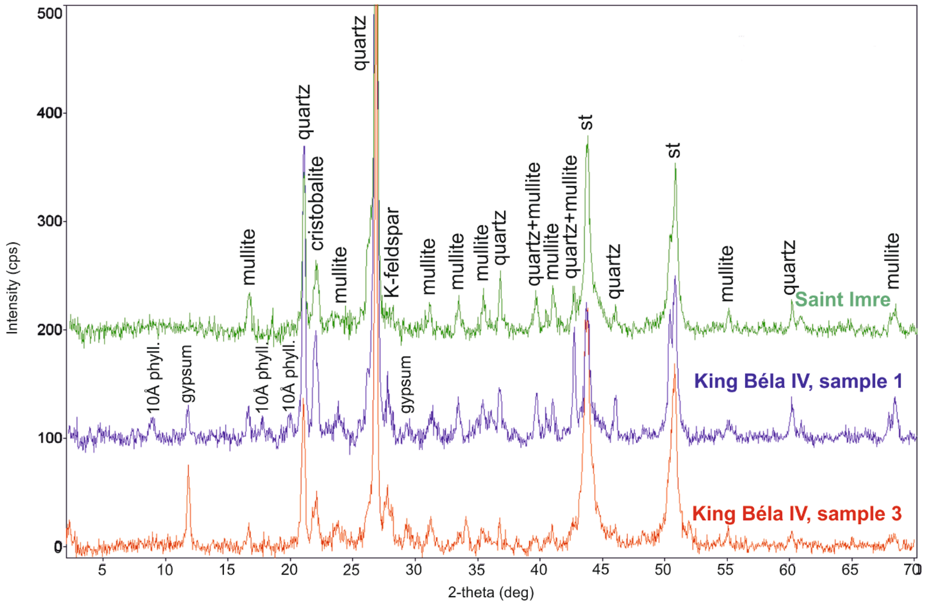

Fig. 2. X-ray diffraction patterns of the pyrogranite ceramic bodies from the back side of the panel (*sample 1)* and from the light blue area of the portrait *(sample 3)* of King Béla IV, as well as from the back side of the Saint Imre panel (st: standard).

pyrogranite ceramic bodies was determined with inductively coupled plasma optical emission spectrometry (ICP-OES). Powdered samples (20–30 mg) were digested by a Multiwave 3000 (Anton-Paar) sample preparation system (microwave digestion) using 8 ml concentrated nitric acid (67%) and 0.5 ml concentrated hydrogen fluoride (40%) solutions. After digestion, 6 ml of a saturated boric acid solution (6%) was added to the samples, and the complexation program was performed with a microwave system to eliminate free fluoride ions. The sample solutions were then washed in 50 ml plastic volumetric flasks with ultrapure water (ELGA PURELAB, 18.2 $M\Omega xcm^{-1}$ water) and were measured by a simultaneous Spectro Genesis ICP-OES equipment with axial plasma observation. The totals of the major and minor elements range from 48.2 to 50.6 wt%. The elemental concentrations were calculated to concentration of oxides, and data were normalised to 100 wt% total.

3. Results

3.1. Ceramic body and white slip

The XRD analysis showed that the light-coloured pyrogranite ceramic bodies of the two experimental paintings (portraits of King Béla IV and Saint Imre) are composed of quartz, cristobalite, mullite and K-feldspar (Fig. 2). All body samples (*sample 1* from the back side of the King Béla IV panel, *sample 3* from the light blue area of the King Béla IV painting and the sample from the back side of the Saint Imre panel) revealed a similar phase composition, albeit in slightly different proportions. Additionally, a small quantity of gypsum was also detected in the body samples from the King Béla IV panel, however, it likely resulted from secondary formation (i.e., contamination), or, alternatively, derived from the white clay slip that covers the pyrogranite body (see below). The phase composition, specifically the presence of mullite and cristobalite, indicates usage of a kaolinitic clay with a significant amount of quartz. Mullite grows at c. 1000–1100 °C during the firing of kaolinitic clays (Heimann, 2010; Gliozzo, 2020 and references therein). Cristobalite typically begins to form from quartz at temperatures above 1000 °C, whereas K-feldspar is thermally stable in non-carbonatic clays up to c. 1200 °C and improves the formation of mullite (Heimann, 2010; Gliozzo, 2020 and references therein). Therefore, a maximum firing temperature of 1200 °C is estimated for the pyrogranite panels.

Based on the ICP-OES measurements, the pyrogranite ceramic bodies are primarily chemically composed of silica and alumina (65–71 wt% SiO_2, 20–24 wt% Al_2O_3), with minor CaO (1.3–4.9 wt%), Fe_2O_3 (1.7–2.6 wt%) and K_2O (1.3–1.9 wt%) (Table 1). The panel of the Saint Imre painting contains less CaO and Fe_2O_3; less iron is due to the white colour of its pyrogranite body, in contrast to the yellowish body colour of the King Béla IV panel.

The pyrogranite panels of the King Béla IV and Saint Imre paintings are porous ceramics, with larger inclusions embedded into a fine-grained matrix (Fig. 3a-c, g-h). The inclusions (non-plastic components) have very inhomogeneous grain sizes up to 300 μm (King Béla IV panel) or 500 μm (Saint Imre panel). They are primarily quartz, but also K-feldspar, other aluminosilicates (probably degraded mica with low K, Ti, Fe and Mg contents), compound particles (e.g., quartz + mica-like? aluminosilicate, quartz + degraded K-feldspar) and, rarely, iron-bearing grains. Additionally, ceramic fragments with sharp and irregular boundaries that are similar in texture and include similar minerals (e.g., quartz) to the rest of the ceramics body also occur (Fig. 3a). Some

Table 1
Chemical composition of the pyrogranite ceramic body of the King Béla IV and Saint Imre panels measured by ICP-OES (in wt%, normalised to 100 wt% total) (*sample 1*: from the back side of the King Béla IV panel, *sample 3*: from the light blue area of the portrait of King Béla IV).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	BaO	Na_2O	K_2O	PbO
King Béla IV, sample 1	65.00	24.34	2.63	0.87	0.02	0.64	4.01	0.05	0.33	1.75	0.36
King Béla IV, sample 3	66.00	20.55	2.34	0.55	0.02	0.43	4.85	0.05	0.57	1.87	2.76
Saint Imre	71.23	19.98	1.72	0.57	0.01	0.30	1.26	0.04	0.61	1.33	2.96

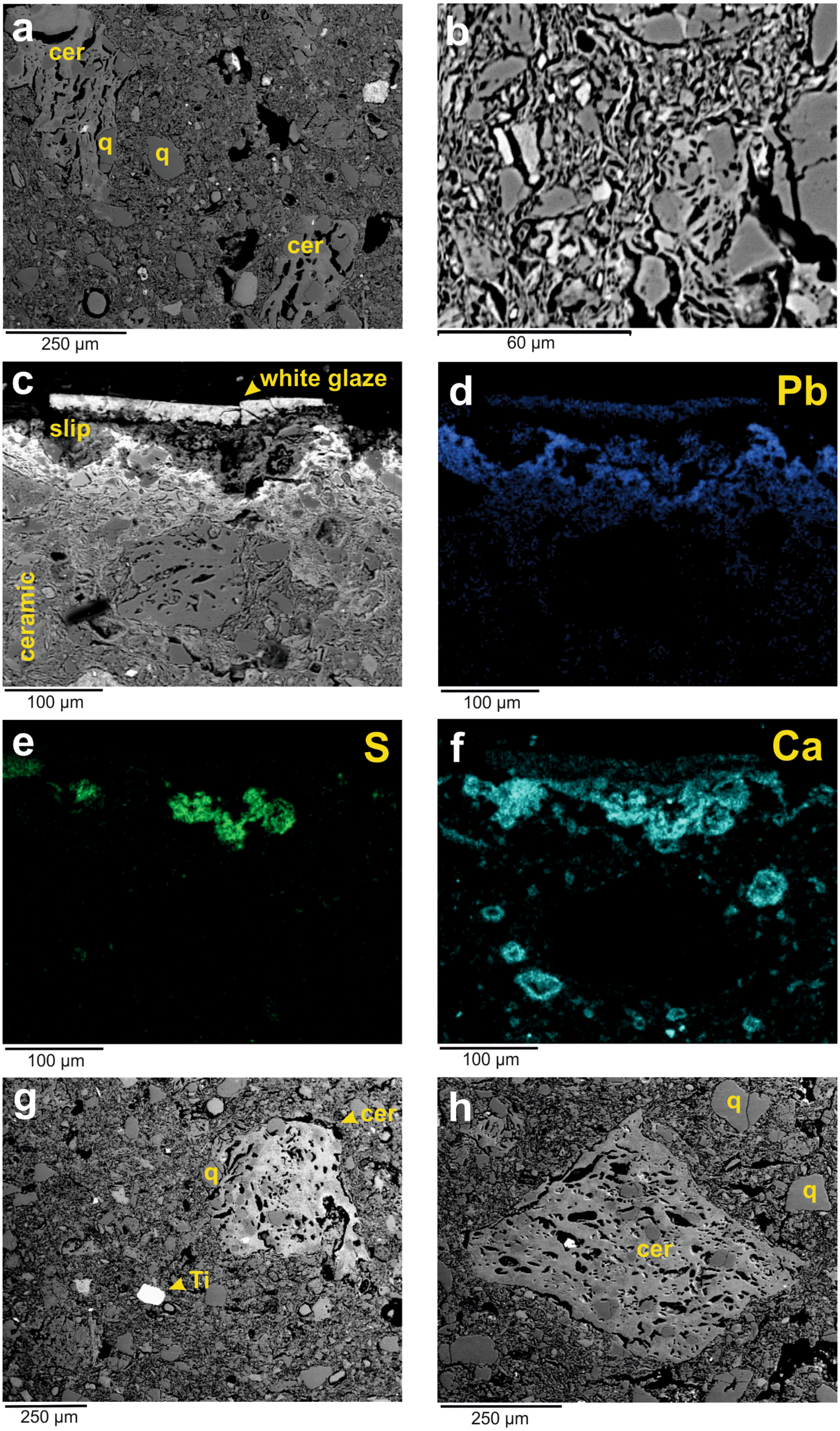

Fig. 3. The King Béla IV panel: a-b) microtexture of the pyrogranite ceramic body (*sample 4*, BSE images), c) ceramic body covered by a slip and the primary white glaze (*sample 3*, BSE image), d-f) X-ray maps showing the distribution of Pb, S and Ca elements, respectively, in the same area as in fig. c; the top part of the ceramic body is lead-rich, whereas the slip is calcium- and sulphur-rich. The Saint Imre panel: g-h) microtexture of the pyrogranite ceramic body (BSE images). Inclusions: q: quartz, cer: ceramic fragment, Ti: titanium oxide.

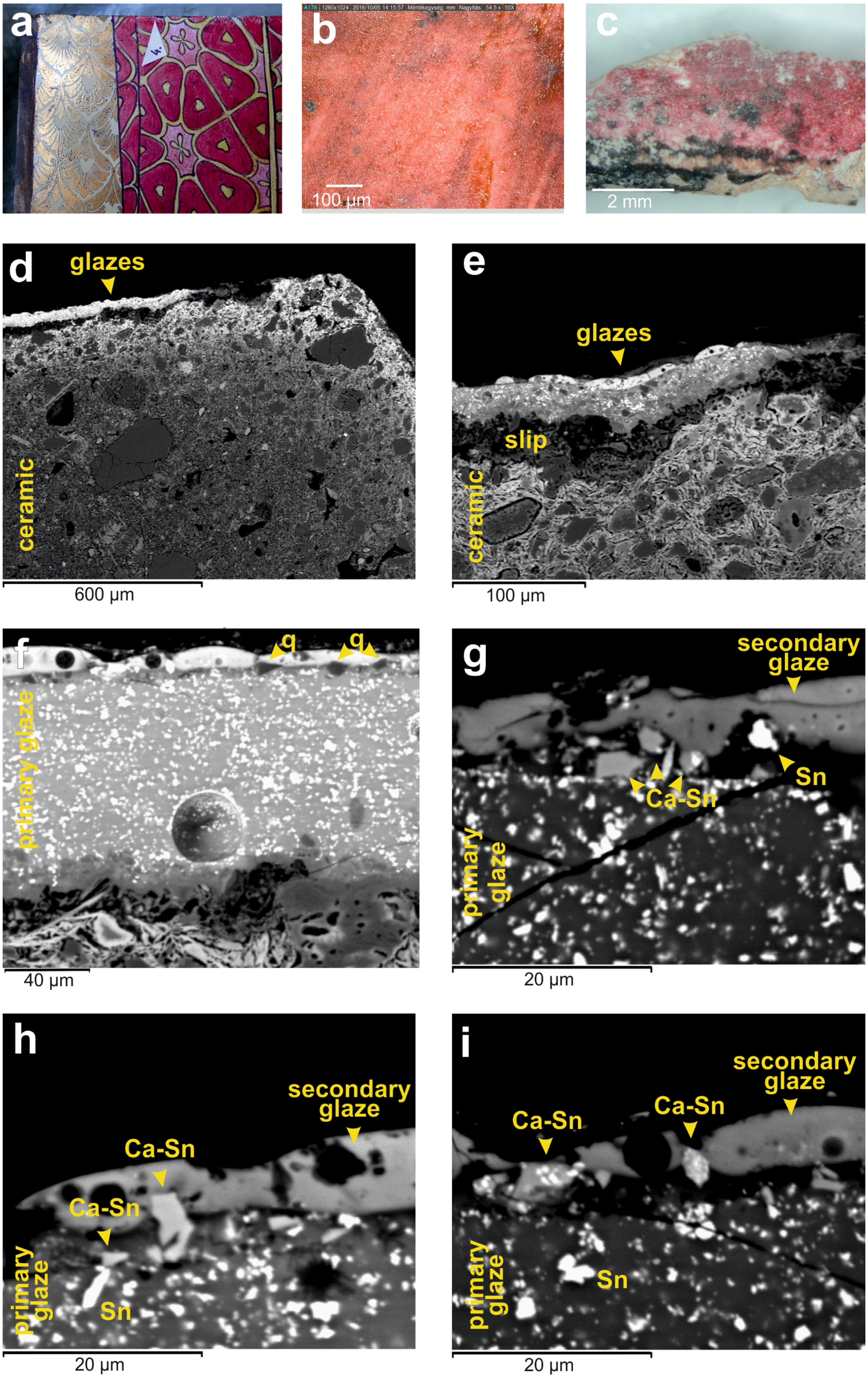

Fig. 4. The King Béla IV painting: a) macroscopic and b) digital microscopy images of red area of the portrait (the clothing), c) stereomicroscopic image of the sample taken from the red area (*sample 4*) (black depositions are contaminations), d-i) microtexture and inclusions of the primary white tin glaze and the secondary transparent glaze, slip was applied atop the ceramic body underneath the primary white tin glaze (BSE images); q: quartz, Sn: tin oxide opacifier, Ca-Sn: calcium-tin silicate pigment (with chromium content) including bright tin oxide grains.

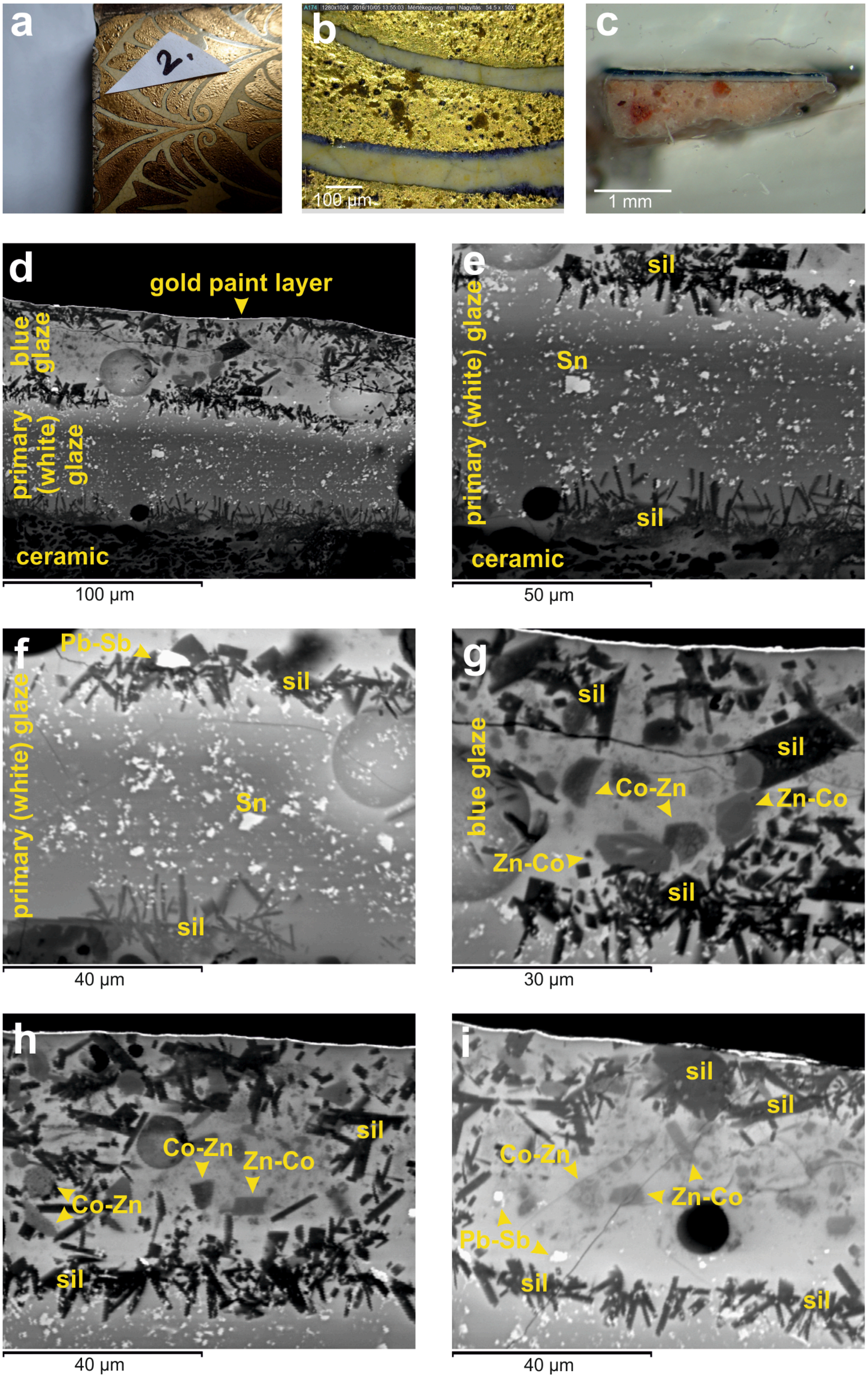

Fig. 5. The King Béla IV painting: a) macroscopic and b) digital microscopy images of golden decorative motifs of the painting, c) cross-section of the glazed ceramic sample taken from a golden motif (*sample 2*), d-i) microtexture and inclusions of the primary white tin glaze applied atop the ceramic body and of the secondary blue glaze covered by a thin layer of gold paint (BSE images); Sn: tin oxide opacifier, Co-Zn: cobalt-zinc ± nickel aluminate pigment, Zn-Co: zinc-cobalt ± nickel silicate pigment, Pb-Sb: lead antimonate pigment, sil: newly-formed aluminosilicate crystals.

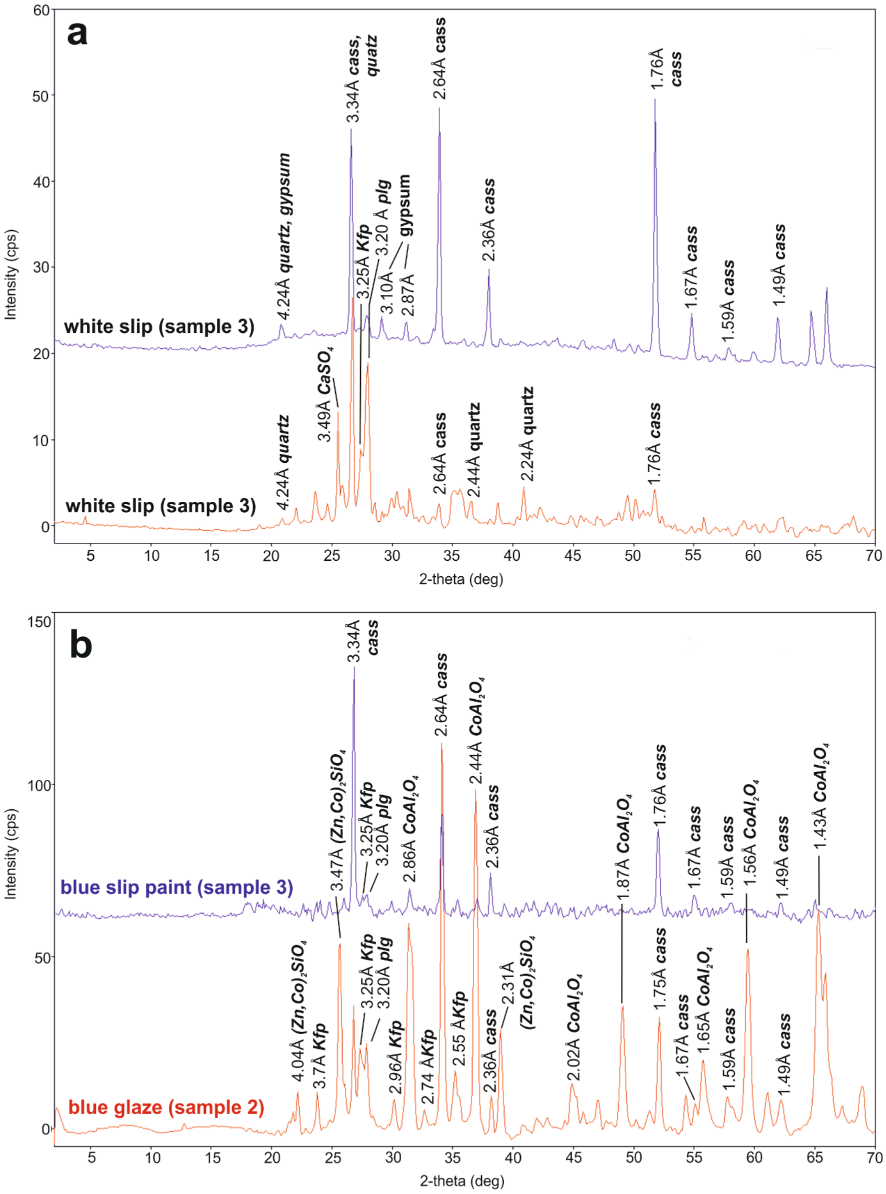

Fig. 6. Micro-X-ray diffraction patterns showing the crystalline compounds a) in the white slip applied atop the pyrogranite ceramic body of the King Béla IV painting (*sample 3*), b) in the blue slip paint layer from the light blue area of the portrait of King Béla IV (*sample 3*) and in the blue glaze underneath the golden decorative motifs surrounding the portrait of King Béla IV (*sample 2*). Detected phases in the white slip: gypsum ($CaSO_4{\cdot}2H_2O$ [PDF 01–074-1904]), anhydrite ($CaSO_4$ [PDF 01–074-2421]), cass – cassiterite (SnO_2 [PDF 01–072-1147] from the overlying white tin glaze), quartz (SiO_2 [PDF 01–086-2237]), Kfp – K-feldspar [PDF 01–089-2650] and plg – plagioclase [PDF 01–083-1371]; in the blue slip paint layer: cass – cassiterite (from the underlying white tin glaze), cobalt aluminium oxide (cubic $CoAl_2O_4$ [PDF 01-82-2242]), Kfp – K-feldspar and plg – plagioclase; and in the blue glaze: cassiterite (from the underlying white tin glaze), cobalt aluminium oxide, cobalt zinc silicate (trigonal $(Zn,Co)_2SiO_4$ [PDF 01–046-1316]), Kfp – K-feldspar and plg – plagioclase.

ceramic fragments are highly vitrified and sometimes contain inclusions (e.g., quartz, Ti- and Ti-Fe-bearing inclusions); the pyrogranite body of the Saint Imre painting contains vitrified fragments in higher amount (Fig. 3g-f). Accessory minerals, such as zircon, barite, apatite and titanium oxide, as well as some bright, lead-bearing grains of up to 20 μm size, are also present. Irregular and elongated pores occur in the matrix and around the grains (Fig. 3b).

The top part (external surface) of the ceramic body of the King Béla IV panel is brighter in the BSE images compared to the interior of the body and to the (slip) layer above it (Fig. 3c-f, Fig. 4d-e), and it contains elevated amounts of lead (up to 38 wt% PbO, based on spot EDX measurements) both in the fine-grained matrix and in the rim of the inclusions. Examination of the glazed body samples from the light blue and red areas of the King Béla IV painting (*samples 3* and *4*) revealed that the ceramic body was covered with a white slip layer of variable thickness (up to 100 μm) (Fig. 3c, 4d-e). This slip layer is not present on the top part of ceramic body under the glazes of the golden decorative motifs (*sample 2*) (Fig. 5), or underneath the glazes of the yellow area of the painting (*sample 5*). The fine-grained slip is primarily composed of silica, alumina and calcium, with small amounts of iron, potassium and sodium, as well as variable amounts of sulphur (21–35 wt% SiO_2, 8.5–14 wt% Al_2O_3, 6.7–10 wt% CaO, 0.5–1 wt% FeO, <0.3 wt% K_2O, <0.3 wt% Na_2O, 0.6–8 wt% SO_3, based on area EDX measurements). No or minimal amounts of lead-bearing grains were detected in this layer, and only up to 2–3 wt% PbO was detected by area EDX measurements. Micro-XRD analysis performed on the white slip layer of *sample 3* shows the presence of calcium sulphate in the form of gypsum or anhydrite, beside cassiterite (SnO_2, from the overlying white tin glaze), quartz, plagioclase and K-feldspar (Fig. 6a). These data indicate that the white slip was probably made of clay mixed with calcium sulphate.

3.2. Glazes and colourants

3.2.1. Microtextural and microchemical analysis

The macroscopic examination of the King Béla IV painting, as well as the microtextural analysis of the cross sections of the glazed ceramic samples revealed that a primary white glaze of up to 100 μm in thickness was applied over the white slip or over the body, if the slip is not present (Figs. 4, 5 and 7). The glaze is a tin-opacified lead type with relatively high amounts of bright, 1–2 μm-sized tin oxide particles and a few, tens of μm-sized rounded pores (Fig. 4f-i, Fig. 5d–f, Fig. 7c–d). Rounded quartz, K-feldspar and calcium aluminosilicate (plagioclase?) inclusions

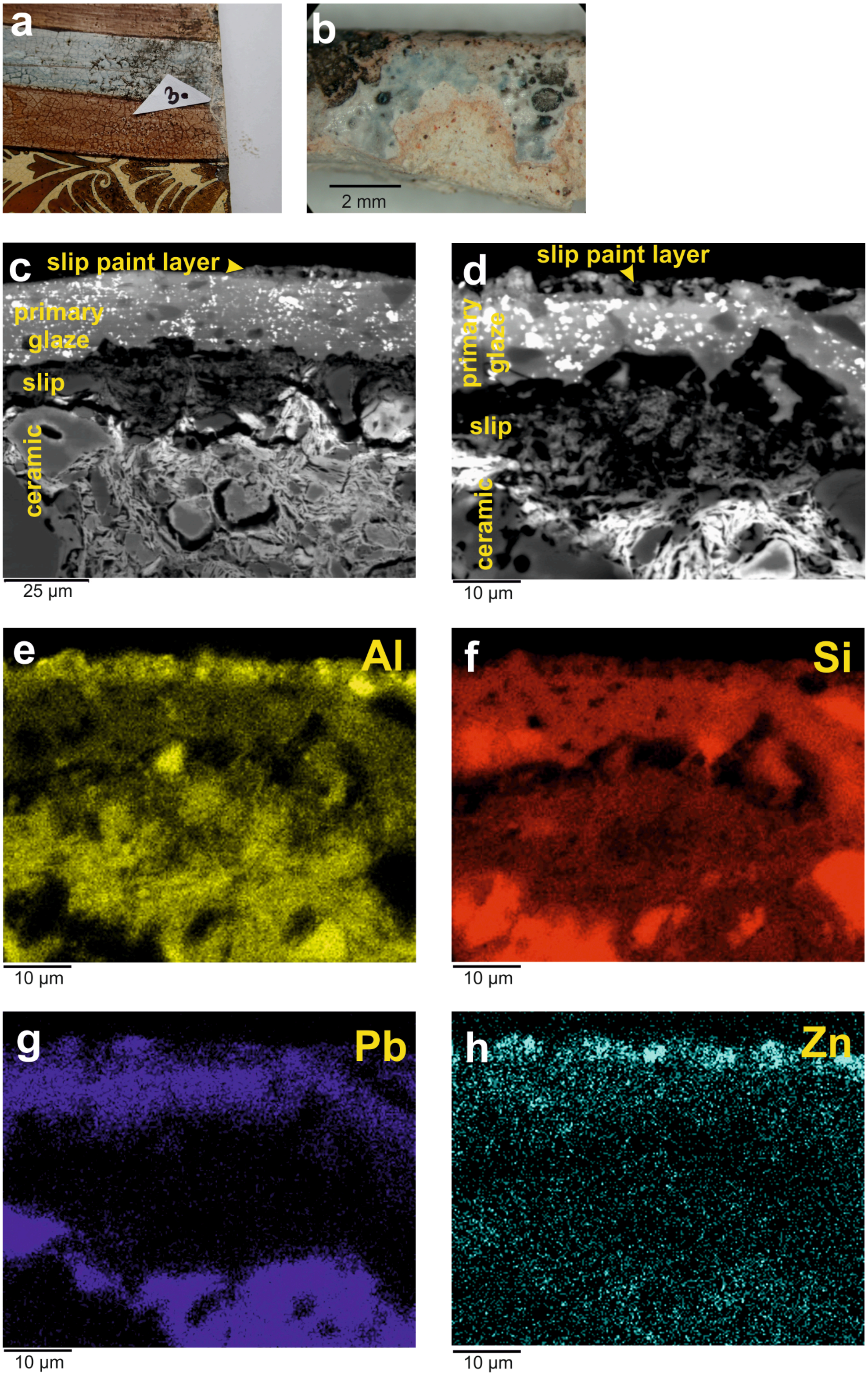

Fig. 7. The King Béla IV painting: a) macroscopic image of light blue area of the portrait of King Béla IV (the clothing), b) stereomicroscopic image of the sample taken from the light blue area (*sample 3*) (black depositions are contaminations), c-d) micro-texture and inclusions of the primary white glaze applied atop the white slip that covers the ceramic body, a porous blue slip paint layer covers the primary glaze (BSE images), e-h) X-ray maps showing the distribution of Al, Si, Pb and Zn elements, respectively, in the blue slip paint layer applied atop the primary white tin glaze in the same area as in fig. d.

Table 2
Chemical composition of the glazes covering the King Béla IV and Saint Imre panels (wt%, area and spot EDX measurements, average ± standard deviation, n = number of measurements).

	SiO_2	PbO	SnO_2	Na_2O	K_2O	CaO	BaO	MgO	Al_2O_3	TiO_2	FeO	CoO	ZnO	Total
King Béla IV														
Glazes under the gold paint layer (sample 2)														
blue glaze (matrix, n = 16)	35.32± 4.81	41.91± 4.21	0.60± 0.46	2.10± 0.15	1.43± 0.44	1.54± 0.25	–	0.22± 0.08	8.48± 1.28	–	0.39± 0.10	2.77± 0.91	5.14± 0.59	99.88± 1.17
primary white glaze (area, n = 4)	47.34± 0.43	20.55± 0.99	14.69± 1.25	2.17± 0.14	3.16± 0.05	1.22± 0.14	–	0.20± 0.03	9.52± 0.34	–	0.33± 0.03	–	–	99.16± 0.83
primary white glaze (matrix, n = 12)	55.09± 1.22	23.89± 1.16	2.53± 1.41	1.59± 0.16	3.59± 0.13	1.53± 0.26	–	0.21± 0.05	10.95± 0.47	–	0.42± 0.06	–	–	99.80± 1.16
Glaze in the light blue area of the portrait (sample 3)														
primary white glaze (area, n = 6)	53.05± 0.77	9.86± 1.14	17.92± 1.53	1.39± 0.05	4.38± 0.17	2.10± 0.40	–	0.18± 0.05	10.34± 0.31	–	0.36± 0.04	–	–	99.57± 0.82
primary white glaze (matrix, n = 8)	62.56± 1.53	12.05± 0.42	4.34± 2.45	1.05± 0.06	5.020.25	2.220.43	–	0.20± 0.05	11.65± 0.46	–	0.39± 0.03	–	–	99.47± 0.49
Glazes in the red area of the portrait (sample 4)														
secondary transparent glaze (matrix, n = 16)	52.99± 1.55	27.89± 2.70	5.00± 1.87	5.30± 0.89	2.92± 0.21	3.39± 0.62	0.61± 0.07	0.27± 0.38	0.95± 0.52	–	0.20± 0.16	–	–	99.50± 1.08
primary white glaze (area, n = 4)	51.11± 1.22	13.44± 1.35	17.31± 0.60	1.87± 0.07	3.76± 0.14	1.76± 0.10	–	0.15± 0.02	9.96± 0.10	0.09± 0.03	0.27± 0.03	–	–	99.70± 0.46
primary white glaze (matrix, n = 22)	60.62± 1.92	16.01± 1.78	2.81± 1.86	1.37± 0.12	4.28± 0.20	2.36± 0.25	–	0.17± 0.05	11.38± 0.42	0.15± 0.05	0.36± 0.05	–	–	99.44± 0.91
Glazes in the yellow area of the portrait (sample 5)														
secondary transparent glaze (matrix, n = 8)	53.55± 2.10	28.18± 3.71	4.63± 2.67	5.12± 0.46	3.17± 0.21	3.11± 0.49	0.64± 0.14	0.14± 0.07	0.66± 0.32	–	0.12± 0.11	–	–	99.27± 1.08
primary white glaze (area, n = 3)	49.44± 1.46	18.85± 2.01	14.84± 0.92	1.78± 0.07	3.76± 0.13	1.28± 0.04	–	0.16± 0.04	9.02± 0.18	0.08± 0.05	0.31± 0.13	–	–	99.73± 0.85
primary white glaze (matrix, n = 16)	57.13± 2.39	21.91± 2.64	2.38± 1.91	1.34± 0.11	4.08± 0.27	1.55± 0.21	–	0.17± 0.04	10.34± 0.59	0.18± 0.08	0.37± 0.11	–	–	99.44± 0.72
Saint Imre														
greyish glaze (area, n = 11)	47.08± 1.32	34.11± 1.72	0.80± 0.11	2.52± 0.34	3.28± 0.15	2.21± 0.12	–	0.17± 0.02	9.12± 0.47	0.11± 0.04	0.18± 0.04	–	–	99.58± 0.86

of up to 10–15 μm are also present in heterogeneous distribution (mainly in the white glaze of *samples 3 and 4*). The glaze has a variable lead content depending on the sample analysed (c. 10–20 wt% PbO in average), with a low total alkali content and high alumina and tin oxide contents (5–6 wt% $Na_2O + K_2O$, 9–10 wt% Al_2O_3, 15–18 wt% SnO_2 in average by area EDX measurements, Table 2). If a slip is not present beneath the primary glaze, there is a c. 20 μm thick interaction layer along the body-glaze interface, with the newly-formed potassium(-sodium-calcium-lead?) aluminosilicate (feldspar?) needles (reaching up to 10 μm in size) growing into the glaze (*sample 2*, Fig. 5d-f).

In contrast, the greyish glaze patches sampled from the back side of the Saint Imre panel exhibit a different microtexture. In addition to rare quartz and K-feldspar inclusions, miniscule amounts of tiny tin oxide particles occur in the glaze (Fig. 8), and dark, <1–5 μm-sized, generally rounded inclusions are abundantly dispersed (Fig. 8b, c). Chemically, these inclusions are composed of calcium and phosphorous, or calcium and sulphur, respectively, indicating that calcium phosphate (apatite) and calcium sulphate are present. The glaze contains higher amount of lead but much lower amount of tin (34 wt% PbO, < 1 wt% SnO_2) than the primary white glaze of the King Béla IV painting, whereas total alkali and alumina contents are nearly similar (6 wt% $Na_2O + K_2O$, 9 wt% Al_2O_3 in average by area EDX measurements, Table 2). The 20–25 μm thick body-glaze interaction zone is composed of many newly formed lead-potassium-sodium-calcium aluminosilicate (feldspar?) needles (Fig. 8). Chemically, two types of needles were identified: darker ones that contain more potassium and sodium, and lighter ones that contain more calcium and lead.

In the red area of the King Béla IV portrait (*sample 4*), the white glaze was unevenly covered by a second, transparent glaze layer, which is much thinner than the primary glaze layer (20 μm maximum thickness)

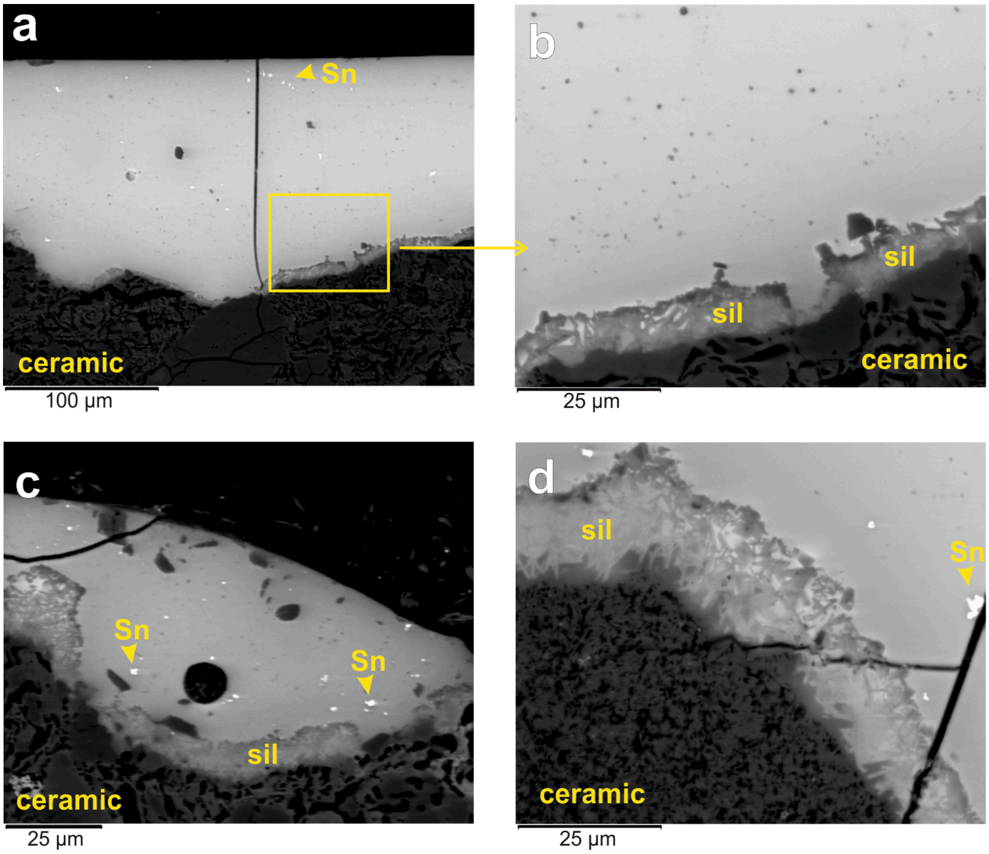

Fig. 8. The Saint Imre painting: a-d) microtexture and inclusions of the greyish glaze covering the ceramic body (BSE images), tiny grey particles in the glaze are composed of calcium and phosphorous, or calcium and sulphur, respectively; Sn: tin oxide opacifier, sil: newly-formed aluminosilicate crystals.

(Fig. 4f-i). The secondary glaze is also different to the primary glaze, because it contains higher amounts of lead and sodium, a much lower amount of alumina and a small amount of barium (28 wt% PbO, 8.3 wt% $Na_2O + K_2O$, 1 wt% Al_2O_3, 0.6 wt% BaO in average by spot EDX measurements, Table 2). Compared to the primary glaze, rounded and irregular pores occur more frequently, as well as, on rare occasions, small tin oxide particles (5 wt% SnO_2 in the matrix by spot EDX measurements). Although the boundary of the two glaze layers is sharp, angular pigment particles and quartz and feldspar grains of up to 10–15 µm occur between the layers and are embedded into them both (Fig. 4f-i). The pigment particles are chromium-bearing calcium-tin silicate grains (c. 20 wt% CaO, 53 wt% SnO_2 and 26 wt% SiO_2 in average with up to 1.5 wt% Cr_2O_3 by matrix-free spot EDX measurements). The particles primarily include brighter tin oxide grains (Fig. 4i), but tin oxide particles occur separately, as well. The calcium-tin silicate particles are comparable to the natural mineral malayaite ($CaSnSiO_5$/$CaSnOSiO_4$).

In the yellow area of the King Béla IV portrait (*sample 5*) a similar layer sequence was found, consisting of a primary tin glaze covered by a secondary lead glaze, the latter of which has a similar composition to that of the secondary glaze in the red area (Table 2). However, discrete pigments or other particles were not found at the sharp boundary of the two glaze layers in the analysed sample, possibly due to sampling at the very edge of the panel, where the yellow paint layer is not present.

The sample from the light blue area of the King Béla IV portrait (*sample 3*) exhibited only the primary white glaze on top of the slip layer; a secondary transparent glaze is not present (Fig. 3c, Fig. 7). Instead, a 5–15 µm-thick, porous slip paint layer composed of angular-subangular grains covers the primary white glaze (Fig. 7). Although these grains are difficult to identify, zinc-cobalt-bearing, tin oxide and some calcium-tin silicate grains are clearly present. Besides cobalt and zinc, X-ray maps show the presence of Al and Si in the slip layer (Fig. 7). Micro-XRD analysis was performed on the blue slip paint layer and identified cassiterite (SnO_2, mostly from the underlying white tin glaze), cobalt aluminium oxide (cubic, $CoAl_2O_4$), K-feldspar and plagioclase (Fig. 6b); cobalt aluminate is the primary pigment responsible for the blue colour (see below).

For the golden decorative motifs surrounding the King Béla IV portrait (*sample 2*), the white tin-opacified lead glaze was covered first by a blue glaze, and then by a thin (1–2 µm) layer of gold paint (Fig. 5a-c). The blue glaze has a thickness similar to that of the primary tin glaze, and the boundary of the two glaze layers is diffuse. The blue glaze contains more lead (42 wt% PbO in average by spot EDX measurements) than the primary white glaze (Table 2). High amounts of alumina, cobalt and zinc were also detected in the vitreous matrix of the blue glaze (8.5 wt% Al_2O_3, 2.8 wt% CoO, 5.1 wt% ZnO, Table 2). Additionally, several angular pigment particles of up to 15 µm occur in the blue glaze, which are cobalt-zinc ± nickel aluminate (19–24 wt% CoO, 9–15 wt% ZnO, 43–53 wt% Al_2O_3, rarely $\sim$ 1.5 wt% NiO) and zinc-cobalt ± nickel silicate (40–58 wt% ZnO, 10–27 wt% CoO, 27–28 wt% SiO_2, rarely < 1 wt% NiO) grains (Fig. 5g-i, for the X-ray maps showing the distribution of Al, Co, K, Pb, Si, Zn and Au elements see Fig. A.1 in the Appendix A). The heterogeneous particles show an aggregated structure in the cobalt-zinc aluminate grains and zonation in the zinc-cobalt silicate grains, with different zones exhibiting different cobalt and zinc contents. A few iron-bearing lead antimonate, lead–tin antimonate and tin oxide particles occur in the blue glaze (Fig. 5f, i), as well. Many newly formed tabular and needle-like potassium-sodium(-barium-lead?) aluminosilicate crystallites of 5–20 µm size are present in the upper part of the secondary blue glaze and particularly in the boundary of the two glaze layers (Fig. 5g-i, Fig. A.1 in the Appendix A). Micro-XRD analysis performed on the blue glaze revealed the presence of cassiterite (SnO_2, from the underlying white tin glaze), cobalt aluminium oxide (cubic, $CoAl_2O_4$),

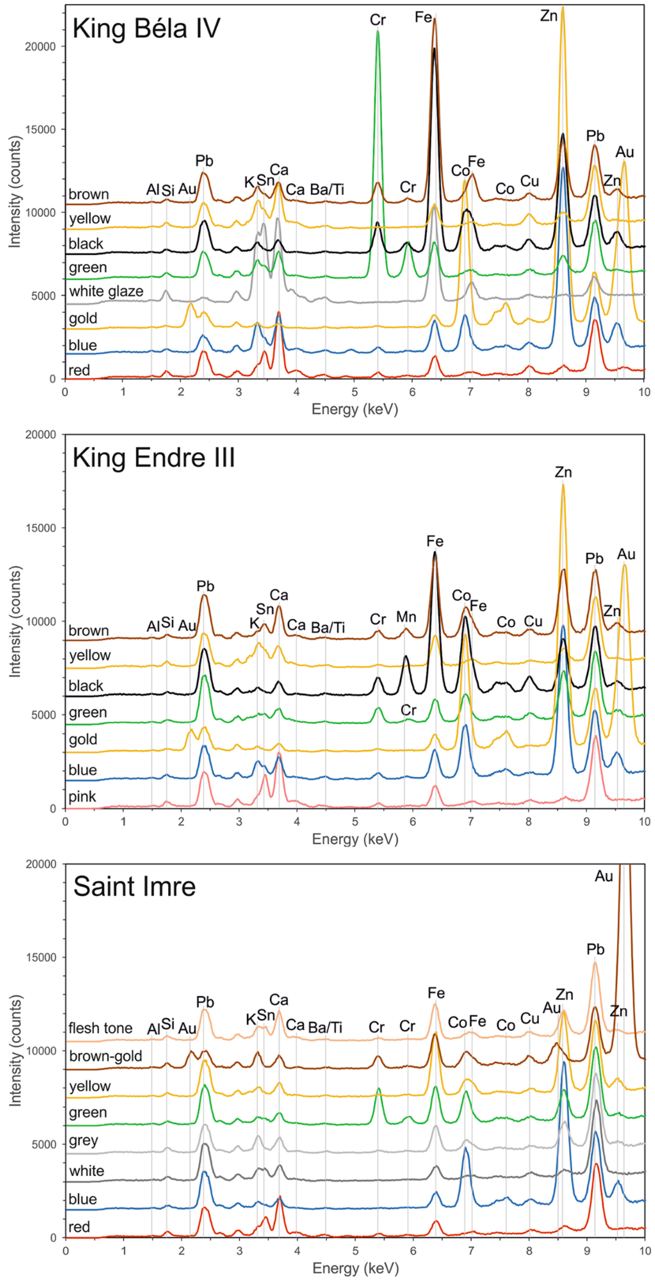

Fig. 9. XRF spectra of the various colours of the three Zsolnay ceramic panel paintings (portraits of King Béla IV, King Endre III, and Saint Imre).

cobalt zinc silicate (trigonal, $(Zn,Co)_2SiO_4$), K-feldspar and plagioclase (Fig. 6b). Although the XRD technique is limited in its ability to discriminate between Co-Al and Co-Al-Zn spinel pigments (Bouchard and Gambardella, 2010), based on the EDX analysis, a mixture of cobalt zinc aluminate and cobalt zinc silicate pigments was used to achieve to colour of the blue glaze.

3.3. *Non-destructive chemical analysis of the panel paintings*

Various colours of the three ceramic panel paintings (King Béla IV, King Endre III and Saint Imre) were analysed non-destructively using handheld XRF equipment to determine the characteristic colourants (Fig. 9). XRF spectra were evaluated qualitatively or semi-quantitatively, based on the relative differences in the peak intensities of the detected elements and the aforementioned results of the glaze samples from the King Béla IV painting (semi-quantitative concentration data of the various colours of the three Zsolnay ceramic panel paintings are shown in Appendix B).

The three paintings exhibit Pb peaks in all spectra, indicating the use of lead-bearing glaze(s). Tin occurs in variable concentrations (8–18 wt % Sn) in the spectra of the various colours of the King Béla IV and King Endre III paintings (9.5–15 wt% Sn in the selected colours of Fig. 9, Appendix B). However, much less tin was detected in the colours of the Saint Imre painting (0.3–1.3 wt% Sn, expect red colour with up to 4.6 wt % Sn content, Appendix B). This difference in tin content indicates that the primary glaze applied over the body (or the slip) of the Saint Imre painting is not same as in the two other paintings, because it contains a much smaller amount of tin.

The red or pink colours in the three ceramic panel paintings are characterised by an elevated tin content compared to other colours, as well as by the presence of chromium (Fig. 9). This is in accordance with the combined use of chromium-bearing malayaite pigment and tin oxide as revealed by the cross sectional analysis of the red area of the King Béla IV portrait. Elevated amounts of cobalt and zinc are present in the blue colour of the three paintings, confirming the use of cobalt- and zinc-bearing pigments. Gold was used in all the three paintings in the decorative motifs surrounding the portraits. In the King Béla IV and Endre III paintings, the gold is accompanied by cobalt and zinc (Fig. 9), which derive from the underlying blue glaze in case of the King Béla IV painting. However, in the Saint Imre painting, the decorative motifs are stylistically different, they are brown in colour and the underlying blue glaze is absent (Fig. 1). Additionally, gold is accompanied by chromium, cobalt and iron(?), but not by zinc (Fig. 9). Thus, a different mixture of colourants including gold was likely used for the Saint Imre painting compared to the other two paintings.

For the green, black, yellow and brown colours we lack direct evidence regarding the colourants from the cross sectional analysis of the glaze samples, but XRF spectra may indicate their characteristic elements. Chromium is enriched in the green colour of the three paintings, particularly in the King Béla IV portrait. Cobalt and zinc are enriched in the green colour of the other two paintings, as well. These elements suggest the use of chromium-bearing pigment(s) mixed with the pigments used for the blue colour. Elevated amounts of chromium, iron, cobalt, copper and zinc are present in the black colour of the King Béla IV portrait, and manganese is also present in the black colour of the King Endre III portrait, implying the use of pigment mixtures. Yellow colour exhibits iron enrichment, which is accompanied by an elevated amount of zinc in the Saint Imre portrait. Interestingly, the spectra of the yellow colour lack peaks that are related to antimony, which would suggest the use of lead(-tin) antimonate, as antimonate pigment particles were detected in the cross section of the blue glaze from the King Béla IV painting. Brown colour is characterised by elevated amounts of chromium, iron and zinc in the King Béla IV portrait and elevated amounts of chromium, manganese, iron, cobalt and zinc in the King Endre III portrait, again implying the use of pigment mixtures.

4. Discussion

Architectural ceramic items, usually referred to as pyrogranite, are produced since the late 19th century by the Zsolnay factory. They are macroscopically variable in colour and texture (Hajtó, 2016). Pyrogranite is often erroneously thought to be fired to compaction and is therefore a hard (“hard as granite”) stoneware, but it is in fact a porous ceramic (Hajtó, 2016). Mattyasovszky-Zsolnay et al. (2005) characterised pyrogranite as a chamotte-bearing “terracotta” (earthenware) with low water absorption, non-conchoidal fracture, high weather resistance and a higher refractoriness than ordinary ceramics. Despite its variability, there is a limited number of published analytical results about the material (phase and chemical) composition and (micro) texture of Zsolnay pyrogranite. Baricza et al. (2015) and Baricza et al. (2016) studied the architectural pyrogranite ceramics (glazed roof tiles) of two buildings in Budapest (Museum of Applied Arts and Geological Institute of Hungary) that were produced during different periods by the Zsolnay factory. Additionally, Czifrák (2008) wrote about the phase composition of the pyrogranite elements of a Zsolnay ornamental duck fountain. Their data and our unpublished analytical data of other Zsolnay pyrogranite items on several Budapest buildings correspond with the results of this paper that similar mineralogical phases (quartz, cristobalite, mullite, K-feldspar, and plagioclase) were detected in other pyrogranite items indicating the use of a kaolinitic clay raw material. A maximum firing temperature of 1200 °C is estimated in this study and was also estimated for the roof tiles by Baricza et al. (2015). The different proportions of the similar mineralogical phases in the roof tiles were regarded as relating primarily to the variation in the raw materials used, rather than to the variation in firing conditions (Baricza et al., 2015). The present data are compatible with some 20th century literature, in which pyrogranite architectural items were described to be ceramic made of fireclay that contained fine-grained quartz, i.e., a mixture dominantly composed of kaolin(ite) and quartz (Mattyasovszky-Zsolnay, 1954; Somodi et al., 1984). Ceramic fragments, such as non-plastic components, were found in the pyrogranite body of the analysed panels, which is in agreement with the literature that states chamotte (fired and ground ceramic made of refractory clay) was added to the clay paste. In the mid-20th century, chamotte grains measuring 1–2 mm were used for tempering in 20 to 40%, and pyrogranite was fired at c. 1300 °C (Mattyasovszky-Zsolnay, 1954).

Lead enrichment that was present in the top part of the ceramic body of the King Béla IV panel was also detected in the outer rims of other Zsolnay products, such as the roof tiles produced at the end of the 19th century (Baricza et al., 2015). This phenomenon is related to the firing of the uncovered (unglazed) panels. During firing of lead-glazed ceramics lead volatiles (Hallse and Cook, 1958; Matousek and Hlavac, 1971; Tite et al., 1998) and lead vapour, which contaminated the kiln used for firing both unglazed and glazed ceramics, diffused into the ceramic body of the unglazed panels.

A white slip composed of clay mixed with calcium sulphate was used to level off the surface of the King Béla IV panel prior to the application of the glaze. The slip could also be applied to hide the yellowish colour of the pyrogranite body. Its lead-free/poor condition indicates that the clay slip was applied after the body was fired. The white clay slip or the ceramic body itself, where the slip is not present, was covered with a white tin (tin-opacified lead) glaze on the entire front surface of the ceramic panel.

The layer sequence of the ceramic painting and the microtextural and microchemical analysis of the layers indicate that the portrait of King Béla IV was created in a different way than were the golden decorative motifs surrounding the portrait. The sample from the red part of the portrait (*sample 4*) revealed identifiable pigment (calcium-tin silicate) and related quartz and feldspar grains on top of the white tin glaze. Additionally, a sample from the light blue part of the portrait (*sample 3*) showed that a thin (5–15 μm) slip paint layer with pigment(s) covered the white tin glaze. Therefore, we postulate that the portrait of King Béla IV was created by means of slip painting, i.e. the use of clay pastes (slips) mixed with colourants (cf. Pradell and Molera, 2020) atop the white tin glaze, after which the portrait was covered by a secondary transparent lead glaze. As slip paint grains are embedded into the white glaze, we propose that coloured slips were likely applied atop the unfired white glaze. The sharp boundary between the primary white tin glaze and the secondary transparent lead glaze, as well as the lack of chromophore elements in the secondary lead glaze indicate that the white glaze, together with coloured slips, was probably fired before the last glaze layer was applied, then the ceramic panel was fired again. Wartha (1892) also stated that the Zsolnay factory created large ceramic panels with colour slips that were used as paints and were fired alongside the base before the final layer of glazing was applied. However, he did not mention the use of a primary tin glaze and was inconsistent regarding the base (raw or fired ceramic body).

In contrast, on the King Béla IV panel, a blue lead glaze, rather than a coloured slip, was applied atop the primary white tin glaze under the top gold paint layer of the motifs surrounding the King Béla IV portrait. The diffuse boundary of the two glaze layers contains several newly formed feldspar crystals, suggesting that these two layers were fired together. The formation of a large number of feldspar crystals requires a high Al_2O_3 content in the glaze; in this case, the alumina was derived from several sources, such as the matrix of the blue glaze, which contained partially dissolved Al-bearing blue pigment particles, and the diffusion of Al from the primary white tin glaze with high alumina content. The latter also explains the preferential precipitation of the feldspar crystals at the boundary of the two glaze layers.

The use of an opaque white tin glaze, i.e., glaze opacified with tin oxide, on a ceramic body has a long history (Caiger-Smith, 1973; Heimann and Maggetti, 2014). Thus, the studied tin-glazed ceramic panels have a wide range of technological precursors, such as the earliest Islamic examples produced in the Near East (8th century CE Egypt and the Levant, Matin et al., 2018); 9th century CE Islamic Mesopotamia (Iraq and western Iran, Mason and Tite, 1997); medieval Islamic pottery, including lustre wares from Iran, Syria, Egypt and Spain (10-14th centuries CE, Molera et al., 2001; Pradell et al., 2008) and Iznik wares from Turkey (Paynter et al., 2004); the Italian maiolica from the 13th-17th centuries CE (Tite, 2009); the tin-glazed earthenware known as faience (faïence), the delftware and majolica from France, Switzerland, Germany, East-Central Europe, the Netherlands and England that were produced until the end of the 19th century CE (see e.g., Maggetti, 2012, 2015; Bajnóczi et al., 2014; van Lookeren Campagne et al., 2018). In contrast to the precursors, in which the white tin glaze was usually applied over a calcium-rich (carbonatic) ceramic body, Zsolnay applied the low-temperature tin-opacified lead glaze atop a relatively high-temperature body (i.e., atop calcium-poor pyrogranite that was fired up to 1200 °C and was covered by a white clay slip). The secondary transparent lead glaze applied on the painting is analogous to the transparent glaze layer applied atop the painted decoration of the Italian maiolica (*coperta*, Tite 2009) and the Dutch tin-glazed pottery (*kwaart*, van Lookeren Campagne et al., 2018). The secondary lead glaze contains more lead than does the primary tin glaze, thus, it is not only a protective coating, but it also served to fill the pores of the coloured slip painting layer beneath and to create a bright, smooth surface, similarly to *coperta* (Tite, 2009). This is in accordance with the descriptions of Mattyasovszky Zsolnay and Hárs (1971) and Zsolnay and M. Zsolnay (1980).

Although tin oxide was used to opacify the primary glaze of the studied ceramic panel paintings, the greyish glaze covering the Saint Imre panel contains less tin oxide compared to the other two paintings, as shown by the microtextural analysis performed on a glazed body sample and by the non-destructive XRF analysis. Additionally, small calcium phosphate (apatite) and calcium sulphate inclusions were detected in the glaze. Their small size and rounded shape indicate that they are remnants of incomplete dissolution during glaze firing. The apatite is possibly derived from the addition of bone ash created by calcining bones. Bone ash acts as an opacifier in glasses (e.g., in late Antique mosaic glass tesserae, Silvestri et al., 2012, 2016) and, less frequently, in glazes (e.g., in Italian maiolica, Viti et al., 2003). The presence of calcium phosphate inclusions is related to the experimentation performed by the Zsolnay factory as some of the tin oxide was substituted with other opacifiers, probably for financial reasons. However, the greyish colour of the glaze covering the Saint Imre panel indicates that opacification was less effective.

In the 19th century, the use of boron (in the form of boric acid or borax (sodium tetraborate)) as a strong flux and network-former (Eppler and Eppler, 2000) became widespread in the creation of low-melting glasses and low-temperature glazes (Speel and Bronke, 2001). Vilmos Zsolnay also used borax to prepare glazes as recorded in his handwritten recipe books. Grofcsik (1971), for example, published some Vilmos Zsolnay's eosin glaze recipes containing boron. However, the EDX spectrometer did not detect boron in any of the studied glazes (white tin glaze, transparent lead glaze, blue glaze underneath the gold paint), because it cannot detect low levels of boron. Other light element-sensitive analytical methods, such as PIGE (Bouquillon et al., 2017, 2018), should be applied to confirm the absence of boron.

Calcium-tin silicate pigment (malayaite) was used as a colourant in the red part of the portrait of King Béla IV. Although malayaite can form *in situ* in glazes (in cobalt- and copper-containing blue, green and turquoise glazes, Coentro et al., 2014, 2017, 2018; Vieira Ferreira et al., 2014; Bajnóczi et al., 2018; Caggiani et al., 2021), in our case, it is an artificial pigment mixed with clay slip and applied between the two glaze layers. Synthetic malayaite is a rare ceramic pigment used to produce pink-red and purple colours. In modern ceramic glazes synthetic malayaite is doped with transition metal ions, primarily with chromium (chrome tin pink sphene – CPMA 12–25-5) (CPMA, 2013; Molinari et al., 2020). Malayaite and tin oxide particles, as well as the incorporated chromium into malayaite aid in the production of red-pink colours (Lee and Lee, 2008). Mattyasovszky-Zsolnay (1954) stated that to prepare the chromium-bearing pink pigment responsible for red colours, Hermann August Seger mixed tin oxide (50 parts), carbonate (25 parts) and quartz (18 parts), and then added saturated solutions of potassium dichromate (3 parts) and borax (4 parts). We found an artificial malayaite pigment that lacked chromium in a modern, 19th century purple glaze used on the restored parts of a Renaissance glazed terracotta statue (Bajnóczi et al., 2018).

Cobalt aluminate pigment was identified as a colourant for the light blue part of the King Béla IV portrait. Additionally, a pigment mixture composed of cobalt zinc aluminate and cobalt zinc silicate was detected in the blue glaze underneath the gold paint layer in the decorative motifs. These pigments were identified as cobalt zinc aluminate blue (cubic spinel-type $(Co,Zn)Al_2O_4$, CPMA 13–28-2) and cobalt zinc silicate blue (trigonal phenacite-type $(Co,Zn)_2SiO_4$, CPMA 7–10-2) (Bouchard and Gambardella, 2010; CPMA, 2013), the latter of which is alternatively called cobalt-doped willemite (Ozel et al., 2010; Molinari et al., 2020). The spinel-type cobalt blue is one of the primary cobalt-containing crystalline structures commonly used in blue pigments, and it was synthetically prepared in the late 18th–early 19th centuries and was commercially manufactured later on (Eastaugh et al., 2008). Blue glaze may have served as a "bole" under the top gold paint layer to enhance its colour, similarly to the gold eosin, which is pale when covers a white glaze, but is bluish gold when it covers a cobalt blue glaze (Mattyasovszky-Zsolnay, 1954). The gold paint layer applied last to the motifs is interpreted as an overglaze or on-glaze paint. To fix the gold paint onto the blue glaze, an additional firing at c. 710–750 °C (Csenkey, 2000) was likely performed, presumably when the transparent lead glaze covering the portrait was also fired, or separately.

The non-destructive XRF analysis of three ceramic paintings (King Béla IV, King Endre III and Saint Imre) reveals that similar pigments were used for red-pink and blue colours in all the paintings, but slightly different colourants, or rather a mixture of colourants, were applied for the other colours, such as green, black and brown. Additionally, the decorative motifs surrounding the Saint Imre portrait were prepared differently using a pigment mixture including gold instead of a blue glaze covered by a thin layer of gold paint. Similarly to the primary glaze, the variability in colourants is explained by the Zsolnay factory's experimentation in order to determine the most suitable form of the colours used to paint the portraits and the surrounding decorative motifs.

5. Conclusions

Although sampling was limited and only one of the large ceramic panel paintings produced by the Zsolnay factory (portrait of King Béla IV) was studied in detail, our study revealed significant information about the production technology and materials used. The porous pyrogranite ceramic panel was covered with a white clay slip. A primary white tin glaze applied over the slip (or the body) served as a "ground" for both the portrait and the surrounding golden decorative motifs. The portrait was created with coloured clay pastes (slips) and covered by a secondary transparent lead glaze (similarly to the Italian maiolica), whereas the golden decorative motifs were produced with a blue glaze that was coloured with cobalt- and zinc-bearing aluminate and silicate pigments, and was covered with a layer of gold paint. Thus, we have shown that the King Béla IV painting employed two different technological methods. Additionally, our research confirms the contemporaneous written sources that state coloured slips were used to paint the portrait. We estimate that during of the production of the ceramic panel paintings, (at least) three or four firings may have occurred.

The non-destructive chemical analysis of three ceramic paintings using a handheld XRF spectrometer revealed slight differences in the materials used, i.e., in the colourants, as well as in the tin content of the primary glaze applied over the white slip. As a result, additional samples from the King Endre III and Saint Imre paintings, as well as further detailed, non-destructive and minimally invasive analyses of other ceramic panel paintings (e.g, those that are displayed and stored in the Zsolnay Museum of the Janus Pannonius Museum in Pécs) may shed more light on the variations in the production technology and in the materials used for the pyrogranite body, the glazes and the colourants.

CRediT authorship contribution statement

Bernadett Bajnóczi: Methodology, Investigation, Visualization, Writing - original draft. **Máté Szabó:** Investigation, Visualization. **Zoltán May:** Investigation. **Péter Rostás:** Conceptualization, Funding acquisition. **Mária Tóth:** Conceptualization, Methodology, Investigation.

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Appendix A

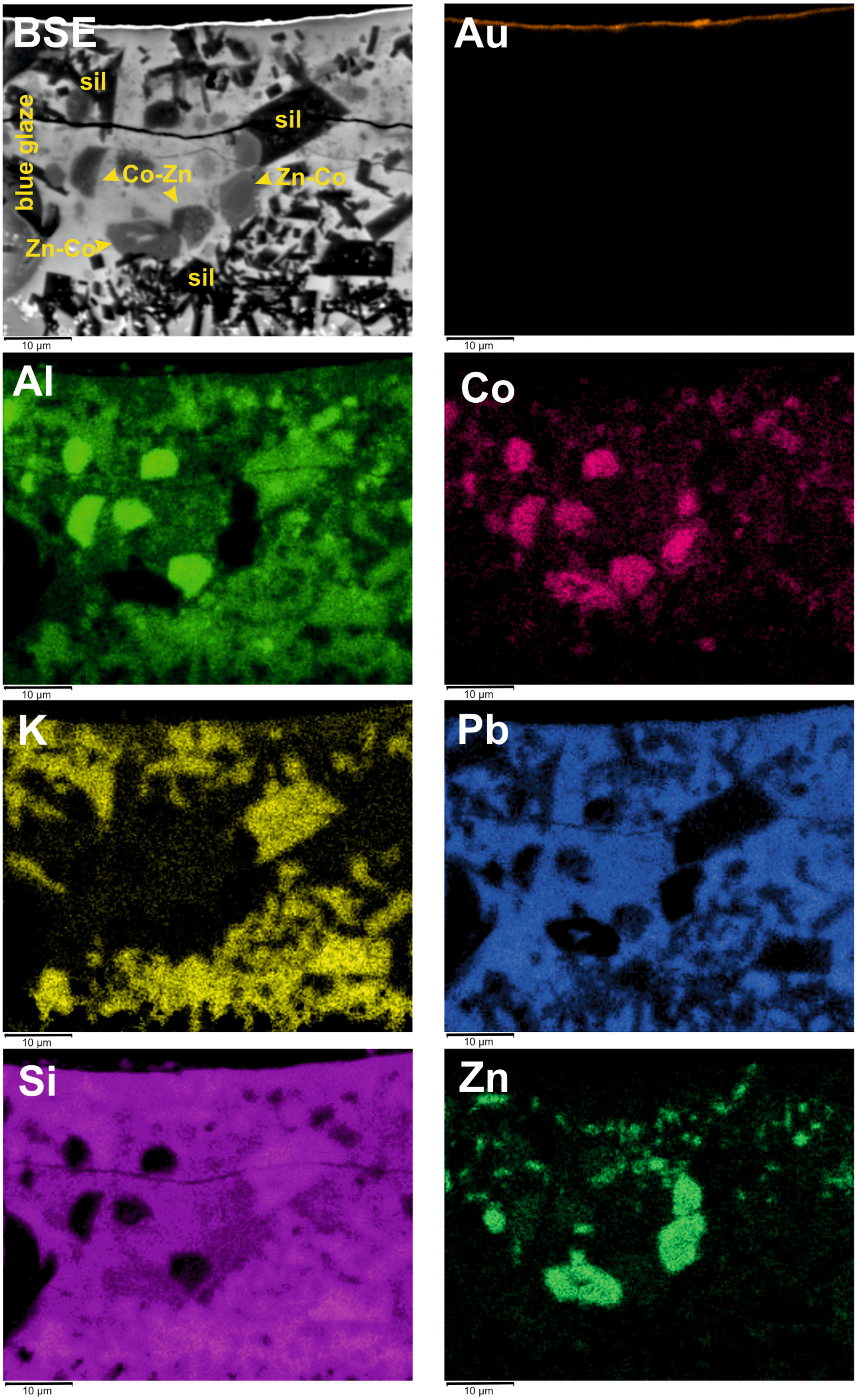

Fig. A1. X-ray maps showing the distribution of Al, Co, K, Pb, Si and Zn elements, respectively, in the blue glaze applied atop the primary white tin glaze, the X-ray map of Au shows the gold paint layer on the top of the blue glaze (*sample 2* from the King Béla IV painting); Co-Zn: cobalt-zinc ± nickel aluminate pigment, Zn-Co: zinc-cobalt ± nickel silicate pigment, sil: newly-formed aluminosilicate crystals.

Appendix B

Elemental concentration values of the various colours of the three Zsolnay ceramic panel paintings (portraits of King Béla IV, King Endre III, and Saint Imre) measured by handheld XRF. Concentrations are given in wt% as shown by the Spectro XRF Analyzer Pro software; impulses (counts, shown in italics and parenthesis) are also given for comparison. Note that Ca and K peaks are indicated in the XRF spectra (Fig. 9), but Ca and K concentrations are not calculated by the 'Light elements' calibration of the instrument (SPECTRO xSORT Combi handheld XRF).

King Béla IV													
No#	Colour	Pb	Sn	Si	Al	Fe	Ti	Zn	Co	Cr	Mn	Cu	Au
1813	red	44.41	14.29	35.60	1.29	0.3339	0.122	0.0137	<0.0059	0.1139	<0.0074	<0.0045	<0.021
		(722769)	*(66376)*	*(91441)*	*(2431)*	*(11277)*	*(1568)*	*(3607)*	*(696)*	*(2715)*	*(379)*	*(4083)*	*(0)*
1815	blue*	43.94	12.54	26.44	12.72	0.715	0.104	<0.017*(0)*	0.9142	0.0926	<0.0065	<0.0038	<0.018
		(673667)	*(54940)*	*(52572)*	*(9261)*	*(17325)*	*(1572)*		*(20043)*	*(2639)*	*(152)*	*(3684)*	*(0)*
1816	green	40.96	9.784	29.05	4.54	0.824	0.034	0.1942	<0.0064	12.52	<0.02*(0)*	<0.0045	<0.020
		(703829)	*(51785)*	*(75464)*	*(4741)*	*(19476)*	*(1236)*	*(10147)*	*(1677)*	*(135130)*		*(2310)*	*(0)*
1818	brown	51.36	11.89	22.15	4.01	6.828	0.039	0.9514	<0.011	1.078	<0.011	<0.0062	<0.025
		(694762)	*(47421)*	*(52267)*	*(4066)*	*(106246)*	*(1133)*	*(31530)*	*(1460)*	*(10807)*	*(0)*	*(1012)*	*(0)*
1819	gold	54.11	9.471	8.09	1.88	0.1289	0.020	6.748	4.559	<0.009	<0.0087	<0.0062	6.98
		(612287)	*(32150)*	*(21969)*	*(2688)*	*(6512)*	*(906)*	*(201088)*	*(86580)*	*(1189)*	*(0)*	*(3113)*	*(72304)*
1821	yellow	44.69	11.30	33.68	6.85	0.3663	0.074	0.0171	<0.0062	<0.0080	<0.0067	<0.0051	<0.021
		(721783)	*(52501)*	*(81915)*	*(6373)*	*(11742)*	*(1356)*	*(3688)*	*(0)*	*(71)*	*(0)*	*(3612)*	*(0)*
1822	black	50.53	11.00	20.03	3.73	7.368	0.063	2.220	0.877	1.653	0.1190	0.0239	<0.026
		(683613)	*(44828)*	*(49476)*	*(3957)*	*(117443)*	*(1196)*	*(70327)*	*(19038)*	*(16296)*	*(2883)*	*(5069)*	*(0)*
2246	white glaze**	1.605	0.4227	31.18	65.52	0.4317	0.0712	<0.00095	0.00708	<0.0015	0.01052	<0.0012	<0.0029
		(280040)	*(37818)*	*(130768)*	*(8663)*	*(55563)*	*(2888)*	*(1635)*	*(1873)*	*(668)*	*(1020)*	*(0)*	*(0)*
King Endre III													
No#	**Colour**	**Pb**	**Sn**	**Si**	**Al**	**Fe**	**Ti**	**Zn**	**Co**	**Cr**	**Mn**	**Cu**	**Au**
1801	pink	50.54	15.09	29.18	2.40	0.3059	<0.016	<0.0048	<0.0064	0.0485	<0.0078	<0.0048	<0.024
		(775044)	*(64635)*	*(77275)*	*(3264)*	*(10209)*	*(876)*	*(2096)*	*(510)*	*(1980)*	*(150)*	*(1469)*	*(0)*
1803	green	61.27	12.95	18.11	2.57	0.422	0.040	0.7150	0.6643	0.810	<0.011	<0.0066	<0.029
		(739980)	*(43756)*	*(42973)*	*(3151)*	*(10661)*	*(1059)*	*(22846)*	*(12913)*	*(7495)*	*(0)*	*(964)*	*(0)*
1804	yellow	52.84	13.39	27.03	3.71	0.586	0.052	0.0086	<0.0073	<0.0092	0.0076	<0.0052	<0.024
		(733246)	*(52223)*	*(63982)*	*(3986)*	*(14048)*	*(1212)*	*(3272)*	*(0)*	*(0)*	*(0)*	*(0)*	*(0)*
1807	gold	55.47	11.90	9.351	1.04	0.2166	<0.015	4.867	3.228	<0.0094	<0.0093	<0.0065	7.318
		(633406)	*(39757)*	*(26106)*	*(2162)*	*(7556)*	*(818)*	*(144905)*	*(60141)*	*(1256)*	*(0)*	*(614)*	*(76260)*
1809	black	58.70	12.07	16.14	1.66	4.710	0.040	0.8445	1.914	0.859	1.508	0.0666	<0.029
		(727863)	*(43459)*	*(38843)*	*(2521)*	*(71133)*	*(1073)*	*(26677)*	*(36109)*	*(8457)*	*(17639)*	*(6025)*	*(0)*
1810	brown	53.96	14.70	22.29	2.70	2.406	<0.016	1.023	0.6242	0.2939	0.2178	0.0058	<0.027
		(745332)	*(57823)*	*(56777)*	*(3342)*	*(40428)*	*(919)*	*(34506)*	*(13552)*	*(3924)*	*(3880)*	*(2025)*	*(0)*
1812	blue	49.01	12.55	23.96	7.63	0.5634	0.150	2.407	1.243	0.1791	<0.0079	<0.0050	<0.025
		(731284)	*(54173)*	*(60078)*	*(6969)*	*(14218)*	*(1571)*	*(83785)*	*(27216)*	*(3116)*	*(585)*	*(1220)*	*(0)*
Saint Imre													
No#	**Colour**	Pb	Sn	**Si**	**Al**	**Fe**	**Ti**	**Zn**	**Co**	**Cr**	**Mn**	**Cu**	**Au**
1825	red	60.40	4.607	32.52	0.633	0.1421	0.057	<0.0052	<0.0065	0.0204	<0.0079	<0.0050	<0.028
		(857925)	*(17876)*	*(91098)*	*(2020)*	*(7237)*	*(1132)*	*(2551)*	*(247)*	*(1618)*	*(276)*	*(1090)*	*(0)*
1829	blue	66.45	0.310	21.41	1.76	0.2139	<0.013	2.649	1.611	<0.0080	<0.0085	<0.0079	<0.035
		(796895)	*(1203)*	*(57708)*	*(2779)*	*(7480)*	*(781)*	*(80206)*	*(30722)*	*(544)*	*(304)*	*(0)*	*(0)*
1831	green	67.43	0.398	21.26	2.06	1.032	<0.015	0.4606	0.7643	1.997	<0.014	<0.0074	<0.035
		(820785)	*(1511)*	*(57243)*	*(3000)*	*(18754)*	*(841)*	*(15837)*	*(15107)*	*(17542)*	*(1175)*	*(0)*	*(0)*
1834	yellow	66.57	<0.043	22.23	2.63	1.979	<0.016	1.323	0.2372	<0.010	<0.010	<0.0072	<0.035
		(789802)	*(242)*	*(57259)*	*(3342)*	*(31687)*	*(856)*	*(40323)*	*(5659)*	*(676)*	*(0)*	*(65)*	*(0)*
1837	flesh tone	60.31	1.338	27.92	3.72	0.855	<0.015	0.3269	<0.0076	<0.0076	<0.0083	<0.0056	<0.030
		(813045)	*(5288)*	*(74398)*	*(4286)*	*(17524)*	*(841)*	*(12878)*	*(1503)*	*(1180)*	*(84)*	*(1736)*	*(0)*
1840	brown (-gold)	44.93	0.314	26.79	4.06	0.7168	<0.013	0.0707	0.2430	0.4726	<0.0091	<0.0062	12.18
		(597303)	*(1418)*	*(80166)*	*(4923)*	*(16461)*	*(787)*	*(5021)*	*(6570)*	*(5908)*	*(0)*	*(2523)*	*(153910)*
1841	white	61.16	0.805	26.30	4.70	0.1289	<0.013	0.0131	<0.0067	<0.0071	<0.0076	<0.0065	<0.030
		(816304)	*(3217)*	*(69725)*	*(5049)*	*(6761)*	*(683)*	*(2961)*	*(1155)*	*(395)*	*(265)*	*(0)*	*(0)*
1843	grey	55.53	0.304	31.93	5.14	0.5183	0.021	0.3383	0.1412	<0.0074	<0.0079	<0.0059	<0.028
		(813189)	*(1435)*	*(91145)*	*(5746)*	*(13026)*	*(949)*	*(13931)*	*(4417)*	*(1134)*	*(345)*	*(0)*	*(0)*

*Zinc is not evaluated by the Spectro XRF Analyzer Pro software, however, elevated peaks of zinc are clearly present in the XRF spectrum of the blue colour compared to other colours (see Fig. 9).

**Concentrations of aluminium, lead and tin were calculated erroneously by the Spectro XRF Analyzer Pro software.

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