

1 **Archaeometric characterization of 17th century tin-glazed Anabaptist (Hutterite)**
2 **faience artefacts from North-East-Hungary**

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13 Abstract

14 The paper presents the first results of a long-term project aiming to reconstruct the production
15 technology of the Anabaptist (Hutterite) tin-glazed ceramics produced in Eastern-Central
16 Europe. Microanalytical investigations were performed on 17th-century faience artefacts (six
17 samples) excavated at Sárospatak, North-East-Hungary. The results are compared with
18 analytical data on the direct or indirect precursor, Italian maiolica.

19 The studied Hutterite faience artefacts reveal similarities with the Italian maiolica.
20 Calcareous clay with 14 to 22 wt% CaO was used for the buff-coloured ceramic body. Up to
21 about 400 µm thick, tin-opacified white and blue lead-alkali glaze was applied on the biscuit-
22 fired body. The glaze suspension contained sand admixture and a significant amount of
23 common salt and was not fritted before application. The colorants used for the ceramic
24 colours are lead antimonate for yellow, cobalt with arsenic, nickel and iron for blue, copper
25 for green and manganese with minor iron for black. The ceramic colours were applied on the
26 unfired glaze and maturing occurred during the second firing. The main technological
27 difference when compared with the Italian Renaissance maiolica is the deliberate use of a
28 high amount of tin oxide (17 to 20 wt% SnO₂) together with 18 to 28 wt% PbO content for
29 white glaze of the studied Hutterite faience.

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31 Keyword: Eastern-Central Europe, Anabaptist, Hutterite, faience, maiolica, tin glaze

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1. Introduction

Production of tin-glazed earthenware (faience) in Eastern-Central Europe was mainly propagated by the Anabaptists in the 16th to 17th centuries. The name “Anabaptist” refers to the third branch of the Reformation (Szebeni, 1998). Anabaptist movement started in the 1520s in Switzerland and quickly diffused to the nearby region of South Germany and the Tyrol. The movement was not united, taking a number of directions with differing viewpoints and degrees of radicalism. The main feature of their religious doctrines, confessional adult baptism and free church organisation resulted in their being from the beginning hunted, executed and forced to leave their homelands. In Eastern-Central Europe the German-speaking Anabaptist communities settled down very early in Moravia, then in the historical territory of Hungary (present-day Slovakia and Hungary) and from 1622 in Transylvania. The first colonies were established in Moravia. In these colonies they began to live in communities of shared property according to the ideas of their leader Jacob Hutter (+1536).

The Hutterites (in Hungary locally called New Christians or latter Habans) excelled in the crafts, among them in pottery production. They started to produce faience alongside their traditional lead-glazed pottery ware in the late 16th century in Moravia (Horvath and Krisztinkovich, 2005; Katona, 1974, 1983, 2001; Kybalová and Novotná, 1982; Pajer, 2007, 2011; Ridovics, 2008). The faience products are mostly white-glazed vessels decorated with flowers and festoons in the late Renaissance style using a reduced, attractive colour palette (yellow, blue, green and purple-black). The Anabaptist ceramic art was formed from particular elements of form, decoration and style of various origins – primarily Italian and Northern Renaissance elements ornamented with Eastern, Persian-Turkish plant motives – reconceptualised in the unique order of Haban pottery. The inspiration of the contemporary Italian maiolica, the “bianchi” di Faenza, highly popular all over Europe, was fundamental (Horvath and Krisztinkovich, 2005; Katona, 1974; Kybalová and Novotná, 1982; Marsilli, 2010; Pajer, 2007, 2011; Ravanelli Guidotti, 1996; Ridovics, 2008; Wilson, 2007). Faience was a high-quality luxury ware produced for high noble families; during the 17th century, especially from the second part, the Anabaptist products slowly spread among wealthy town people, minor nobility and members of the guilds as well. At the end of the 17th century Hutterite colonies started to disintegrate, and by the middle of the 18th century people were either being forced to convert to Catholicism and assimilated into the local population or they emigrated. The art of Anabaptist ceramic production was preserved in folk pottery as well as in the artistic faience ware produced by manufactures.

1 It is not certain from where the know-how of tin glazed pottery, the inspiration for the
2 application of the faience technique in the Anabaptist ceramic workshops, has originated.
3 Some researchers suggest the possibility that Anabaptist faience has a direct relationship with
4 Italian maiolica. The tin-glaze technique had been brought by refugees (emigrants) from
5 North Italy (e.g. Faenza) who joined their co-religionists in Moravia (Kybalova, 1995;
6 Kybalová and Novotná, 1982; Marsilli, 1985, 2010). Other scholars (e.g. Pajer, 2007, 2011)
7 think it more likely that the Italian influence was mediated and indirect, the direct source of
8 inspiration being from a geographically and culturally closer region, probably South
9 Germany, where this technology already existed in the 16th century.

10 While the production technology and the materials used for the Italian Renaissance
11 maiolica are fairly well known thanks to Cipriano Piccolpasso's treatise on the potter's art
12 written circa 1557 (Lightbown and Caiger-Smith, 2007) and to extensive archaeometric
13 research (see the recent comprehensive paper published by Tite, 2009), similar sources are not
14 available for Hutterite faience. No contemporary written documents are known about the
15 production technology. A potter's diary reporting recipes of some Haban white and coloured
16 glazes is known (Wartha, 1892); however, recipes were recorded later, only at the beginning
17 of the 19th century. Systematic archaeometric investigation on Hutterite faience using modern
18 analytical techniques has not yet been performed either in Hungary or other countries. Only a
19 very few tin-glazed, lead-glazed and unglazed Hutterite archaeological ceramic artefacts from
20 Southern Moravia have been analysed to date (Gregerová et al., 2007; Kuljovská, 2007;
21 Trojek et al., 2010).

22 Our archaeometric research aims to identify the raw materials used for the body, the
23 glaze and the decoration (colours) as well as the reconstruction of the production technology
24 (i.e. the firing conditions, the preparation method of the glaze). Today numerous public and
25 private collections hold Hutterite-Haban ceramic objects (from the period of appr. 1593 to
26 1750), several hundreds of items exist. But due to the good quality of preservation, sampling
27 of these museum and collection objects is usually limited. We therefore mainly focus on
28 archaeological artefacts, which have previously gained little attention in Hungarian research.

29 This study presents the result of the microanalytical investigations performed on
30 Hutterite faience fragments excavated at Sárospatak (NE Hungary, Fig. 1). Six samples were
31 analysed in the first step of the archaeometric research. They obviously do not give a
32 comprehensive overview of the whole Anabaptist faience production existing over circa one-
33 and-a-half centuries in several production centres of Eastern-Central Europe. However, even
34 these six analysed samples provide an interesting idea about the technology, especially if we

1 compare the results with the previously published analytical data of the possible model,
2 Italian maiolica.

3

4 2. Materials and methods

5 2.1 Samples

6 In 2006 the team of the Rákóczi Museum of the Hungarian National Museum started the
7 excavation of the remnants of a gun-foundry in the outer castle of Sárospatak (NE Hungary,
8 Fig. 1) (Ringer, 2011). According to written sources (Détshy, 1970) the gun-foundry
9 functioned in the 17th century, between 1631 and 1648 and was most probably destroyed by a
10 fire in 1672. Fragments of Anabaptist faience objects were found in the late 17th century
11 infillings of the remnants, at several occurrences, mainly in the southern part of the gun-
12 foundry.

13 In the frame of this study six samples from different faience objects were analysed
14 (inventory numbers: sample 1: SRM 2010.07.15.1, sample 2: SRM 2010.07.15.2, sample 3:
15 SRM 2010.06.25.1, sample 4: SRM 2010.06.22.1, sample 5: SRM 2010.06.24.2, sample 6:
16 SRM 2010.06.23.1). The studied artefacts are mainly white-glazed ceramics: a fragment of a
17 jug (Fig. 2a; sample 1) and fragments of several other objects, most probably bowls (Fig. 2b,
18 c, d, e; samples 2, 3, 4, 5). Also found was a fragment of a tazza with opaque blue glaze on
19 the stand and on the external side of the dish and white glaze on the internal side of the dish
20 (Fig. 2f; sample 6). Several fragments of the objects, especially of the bowls, were found (Fig.
21 2b, c, d), and one fragment of each object was chosen for detailed study. Both sides of the
22 objects are glazed and half of the analysed shards are non-decorated (samples 3, 4, and 5). On
23 one side of the other artefacts there are blue, yellow, green and black decorations (samples 1,
24 2 and 6); they represent all the decoration colours used for Hutterite faience (Fig. 2).
25 Decorative motives, e.g. the blue lace motif on sample 1 (Fig. 2a), black numbers on sample 2
26 (Fig. 2b) or the blue ornaments on sample 6 (Fig. 2d) are typical of Hutterite faience.

27 These artefacts were chosen for study due to their possible local provenance. Written
28 sources documented that in 1645 Prince György I. Rákóczi invited Hutterites from Csejte
29 (today Čachtice in Slovakia) to Sárospatak (Román, 1955, 1959). The Hutterite colony in
30 Sárospatak existed until c. 1680 when due to conversion to Catholicism it was dissolved, the
31 craftsmen emigrated or were assimilated into the local community. The colony had a ceramic
32 workshop operated by one master and four assistants (Román, 1959). Figure 75 drawn on
33 sample 2 (Fig. 2b) indicate most likely the date of production, i.e. 1675, which would fit in
34 with the active period of the local Hutterite ceramic workshop. However, archaeological

1 excavation of the local Hutterite settlement with the ceramic workshop has only started
2 recently (in 2010) and until now ceramic finds have not been analysed. Therefore the
3 provenance of the studied faience fragments based on the comparison with the local Hutterite
4 products cannot currently be determined.

5

6 2.2 Analytical methods

7 From the selected samples, after washing with water polished cross-sections were made from
8 slices cut perpendicular to the glaze-ceramic body interface. After coating the cross-sections
9 with carbon, the microstructure of the ceramic body, glaze and colours was examined using
10 the backscattered electron (BSE) mode of a Zeiss EVO MA 15 scanning electron microscope
11 (SEM) and a JEOL Superprobe-733 electron microprobe.

12 The 'bulk' chemical composition of the body, the glaze and the colours were
13 determined using an Oxford Instruments Inca Energy 200 energy dispersive spectrometer
14 (EDS) attached to the electron microprobe, run at 20 keV and 6 nA. During quantitative EDS
15 analyses natural and artificial materials were used as standards. For the ceramic body,
16 standards provided by the Taylor Co. (USA) were used: quartz for Si, corundum for Al,
17 wollastonite for Ca, magnesium oxide for Mg, albite for Na, orthoclase for K, hematite for Fe
18 and rutile for Ti. For the glaze and the colours well-known artificial glasses (NMNH 117218-
19 4, -1, -2, -3, i.e. Corning archaeological reference glasses A, B, C and D, Vicenzi et al., 2002)
20 were used as standards for the main elements, while SnO₂ for Sn, pure metals for Co and Ni,
21 gallium arsenate for As, chalcopyrite for Cu and antimony telluride for Sb were applied. For
22 all the 'bulk' measurements the count time was 100 seconds. PAP correction was
23 automatically made by the Oxford Instruments software. The method is not able to distinguish
24 between oxidation states of polyvalent elements; therefore all iron is expressed as FeO and all
25 manganese as MnO. The detection limits of the spot (matrix) analyses is about 0.2 to 0.3 wt%
26 for most elements, but not better than 0.4 wt% for CuO and As₂O₃, 0.5 wt% for Sb₂O₃ and 0.6
27 wt% for SnO₂. The limits of the areal analyses are lower by a factor of 0.63.

28 The area of 'bulk' EDS analyses for the ceramic body was 1000 × 1000 μm. On the
29 other hand, the analysed areas of the glaze and the colours were set as large as possible
30 depending on glaze/colour thickness and on the density of pores and cracks that have been
31 eliminated as far as possible. The areas varied from 66 × 66 μm to 250 × 250 μm for the glaze
32 and from 30 × 30 μm to 185 × 185 μm for the colours. Typical inclusions, such as quartz,
33 feldspar, tin oxide and pigment particles, were included in the analysed area, but the body-
34 glaze interface and the outermost part of the glaze were avoided. At least three area

1 measurements were performed on each body and glaze and the results were averaged. In
2 addition, several spot analyses were performed for the determination of glassy matrix
3 composition. During analysis the stability of beam/specimen current was repeatedly checked.
4 The analytical totals of the body are between 67 and 78 wt%. There are several reasons for
5 low totals of the quantitative analyses of ceramics (Ionescu et al., 2011); in this study the low
6 totals are related to the high porosity of the body. The analytical totals of the glaze and the
7 colours vary in the range of 88 and 100 wt% for various reasons, e.g. pores (and sometimes
8 cracks), the possible presence of components that cannot be analysed and the analytical
9 uncertainties. All analytical data were normalised to 100%. The glaze was analysed on both
10 sides of the objects and no significant differences were detected, therefore we report here only
11 the chemical compositions measured on the glaze under the decorations or on the thicker
12 glaze. The chemical composition of the colour pigments was also measured using spot EDS
13 analyses.

14 Phase composition of the ceramic body, the glaze and the yellow colour was
15 determined on powdered samples (circa several hundred milligrams) by X-ray diffraction
16 analysis (XRD) using a PHILIPS PW 1730 diffractometer in Bragg-Brentano geometry
17 (instrumental and measuring parameters: $\text{CuK}\alpha$ radiation, $2\text{-}70^\circ$ range of 2θ scanning,
18 45kV acceleration voltage, 35 mA tube current, 1 sec/ 0.05° 2θ data collection speed, graphite
19 monochromator).

20 The colour pigments were identified by using Raman microspectroscopic analysis on
21 the polished cross-sections using a HORIBA JobinYvon LabRAM HR800 dispersive, edge-
22 filter based confocal Raman spectrometer (focal length: 800 mm) equipped with an Olympus
23 BXF_M microscope. The spectra were collected using the 632.8 nm emission of a He-Ne red
24 laser, a 100 \times (N.A. 0.9) objective, a grating with 600 grooves/mm and a pinhole of 100 μm ,
25 which also acted as the entrance slit to the spectrometer. The Raman spectra of the inclusions
26 were compared with the reference spectra of mineral phases of the RRUFF Project database
27 (<http://rruff.info>).

28

29 3. Results

30 3.1 Ceramic body

31 The XRD analysis revealed that the ceramic body of the artefacts is generally composed of
32 quartz, gehlenite, diopside, plagioclase, sometimes K-feldspar, hematite and traces of 10 Å
33 phyllosilicate (illite) (Fig. 3a). Calcite was detected in only two samples (samples 1 and 6).

1 The BSE images indicate that the body has high porosity (Fig. 3b, c). Mainly quartz,
2 K-feldspar, mica (biotite, muscovite), accessory minerals (e.g. apatite, zircon, Ti-oxide,
3 monacite, ilmenite, garnet) and composite particles (e.g. quartz+K-feldspar, K-
4 feldspar+biotite, quartz+mica) occur in the matrix, their sizes ranging from several up to 300
5 μm . Regarding the type, the quantity and the size of particles the samples show no noticeable
6 difference. Only some tiny, discrete Pb±Sb-bearing particles occur in the body of sample 1;
7 these were (most likely randomly) added to the clay before firing. Carbonate (calcite)
8 particles of several tens of μm size rarely occur, but most frequently voids due to the
9 dissociation of carbonate are present (Fig. 3b, c). Spot EDS analyses indicate the enrichment
10 of calcium in the fine network of the matrix and around the particles. According to ‘bulk’
11 chemical analyses by EDS the ceramic body has 14.2 to 22.5 wt% CaO accompanied by 3.9
12 to 5.4 wt% FeO content (Table 1).

13 The glaze-ceramic body interface is usually sharp; no intermediate zone is visible.
14 Only a small amount of newly-formed, acicular Ca-rich phases (wollastonite?) of 2-3 μm size
15 were detected at and near the glaze-body boundary suggesting that the interaction between the
16 body and the glaze was usually limited.

17

18 3.2 Tin glaze

19 The tin-opacified glaze covering the artefacts includes two types: the white one (all samples)
20 and the blue one (sample 6 only).

21 The white glaze has a thickness of 170 to 430 μm on the front/decorated side in the
22 studied cross-sections, except on sample 6, where the white glaze is 100 to 150 μm thick. The
23 white glaze is thinner on the reverse/non-decorated side (140 to 250 μm). All of the white
24 glazes contain high amounts of inclusions and rounded pores heterogeneously distributed in
25 the vitreous matrix (Fig. 4a). The size of the pores usually ranges from several to 60 μm ,
26 sometimes up to 120 μm . The inclusions are mainly cassiterite particles and varying amounts
27 of angular to rounded quartz and potassium feldspar grains up to 60 μm size. BSE images
28 show two types of cassiterite in the white glaze (Fig. 4b): relatively large (up to 10 μm size)
29 angular particles as well as small needles (up to 1-2 μm size) and aggregates of needles (up to
30 40 μm size) occur. In several cases the close intergrowth of the two types of cassiterite is
31 clearly visible (Fig. 4b).

32 The ‘bulk’ compositions of the white glaze measured by EDS (Table 2) indicate that
33 according to classification of Tite et al. (1998) it is a lead-alkali glaze with 22 to 28 wt% PbO
34 content (except sample 4 with 18 wt% PbO content) and 5.8 to 7.4 wt% total alkali

1 (Na₂O+K₂O) content. The SnO₂ content ranging from 16.9 to 20.3 wt% confirms the high
2 amount of cassiterite visible on the BSE images. Spot analyses of the glaze matrix show SnO₂
3 values of up to 6 wt%. The Na₂O content is greater than or equal with the K₂O content in the
4 'bulk' white glaze and the K₂O/Na₂O ratio is relatively low (0.5 to 1.0), except for sample 6,
5 where the Na₂O content is lower than the K₂O content, and the K₂O/Na₂O ratio is 1.8.
6 Chlorine has detectable amounts up to 1 wt% in the tin glaze.

7 The microstructure of the tin-opacified blue glaze is similar to the white glaze with
8 fewer quartz and feldspar particles (Fig. 4c). The thickness of the blue tin glaze varies
9 between 180 and ~300 μm and it is also of lead-alkali type with 28 wt% PbO, 8 wt% total
10 alkali content and K₂O/Na₂O ratio of 1.6 (Table 2). Both types of cassiterite are present, but
11 the SnO₂ content is lower (11 wt%, Table 2) than that of the white glaze on the same object
12 (sample 6). The presence of significant CoO content (~0.7 wt%) associated with As₂O₃ (0.86
13 wt%) and some NiO (0.16 wt%) (Table 2), as well as the calcium-lead arsenate crystals
14 preferentially deposited inside the pores (Fig. 4d) and also dispersed within the glassy matrix,
15 indicate the use of cobalt colorant for the blue glaze.

16

17 3.3 Decorations

18 The yellow, blue, green and black ceramic colours were applied as paintings on the tin-
19 opacified white glaze. The paintings can be as thick as the glaze (Fig. 5), their thickness
20 sometimes exceeding 300 μm. The ceramic colours consist of coloured glass containing in
21 'bulk' more SiO₂ (38 to 56 wt%) than PbO (22 to 37 wt%) and the total alkali contents range
22 from 6.5 to 9 wt% with K₂O/Na₂O ratio from 0.5 to 1.4 (Table 3). The SiO₂ and PbO contents
23 as well as the alkali content of the vitreous matrix of the different colours vary considerably
24 among the studied samples. Chlorine is present in the colours in concentrations of up to 1
25 wt%.

26 The yellow colour is opaque due to the presence of a high number of angular, few μm
27 size, antimony-bearing pigment particles (Fig. 6a, b). The pigment is lead antimonate
28 indicated by EDS spectra and confirmed by XRD. The Raman spectra of the lead antimonate
29 particles (Fig. 7a) show an intensive band at about 510 cm⁻¹ along with peaks at 330-340 and
30 460 cm⁻¹ indicating that the original pyrochlore structure is distorted due to substitution of
31 antimony by a larger cation like Zn, Sn or excess Pb (Rosi et al., 2009, 2011). However, in the
32 studied yellow colour the structure of lead antimonate is probably modified by other cations:
33 EDS spectra indicate iron, calcium and sodium as minor components in the lead antimonate
34 pigment (e.g. in sample 1 up to 3.5 wt% FeO, 2.8 wt% CaO, 1.8 wt% Na₂O). The vitreous

1 matrix of the yellow colour has a small amount of antimony (especially in sample 1 with 1.2
2 wt% Sb_2O_3 , Table 3). Slightly elevated iron content compared to that of the white glaze was
3 also detected (≥ 2 wt% FeO , Table 3). The colour shows two different microstructures. In
4 sample 1 pigment particles are distributed heterogeneously, frequently aggregating into
5 clusters, with a few quartz and feldspars particles and relatively large pores occurring (Fig.
6 6a), while in sample 2 pigment particles are distributed homogeneously accompanied by
7 higher quantities of quartz and feldspar particles and smaller pores (Fig 6b). Tin oxide may be
8 present only in very small amounts in the yellow glaze of sample 2 (0.86 wt% SnO_2 , Table 3).

9 Similarly to the tin-opacified blue glaze, the blue colour contains cobalt colorant (up to
10 1.4 wt% CoO) dissolved in the vitreous matrix accompanied with comparable concentrations
11 of nickel and arsenic (up to 0.9 wt% NiO and 1.7 wt% As_2O_3 , Table 3); discrete pigment
12 particles were not identified. Slightly elevated iron content (1.1 to 1.4 wt% FeO) is
13 characteristic compared to the white glaze. The blue colour may contain a small number of
14 cassiterite particles if it is directly applied over the white glaze (Fig. 6c); also the underlying
15 white glaze contains some cobalt and arsenic above detection limit (Table 2). Tiny arsenate
16 crystals together with small-sized quartz particles and silica flakes (probably newly formed
17 cristobalite) occur scattered in the vitreous matrix of the blue painting of sample 2 (Fig. 6d).

18 The green contains copper dissolved in the matrix as colorant (1 to 2 wt% CuO , Table
19 3). A few lead antimonate particles occur in the green colour of sample 1; however, its 'bulk'
20 Sb_2O_3 content is very low (0.2 wt% Sb_2O_3). In both samples 1 and 6 the green colour is
21 opaque due to the presence of abundant, homogeneously distributed cassiterite particles (Fig
22 8a). The SnO_2 content is 13.8 and 11 wt%, respectively (Table 3) which is lower than that of
23 the white tin glaze applied on the same object, but in a range similar to that of the blue tin
24 glaze applied on sample 6. In addition, the green colour of sample 6 contains some traces of
25 quartz and feldspars. The white glaze under the green colour contains copper colorant (0.6 to
26 1.5 wt% CuO).

27 The black is usually applied as the last decoration, as e.g. contour lines (Fig. 2, 5).
28 Black is associated with manganese, which is present in two forms: as an ionic colorant in the
29 vitreous matrix (Table 3), and as discrete pigment particles. Rhombic manganese silicate
30 crystals up to 5-6 μm size occur in the black colour of samples 1 and 6 (Fig. 8b, c). Raman
31 microspectroscopic analysis shows the manganese silicate crystals to be braunite (Fig. 7b).
32 Porous crystal aggregates up to 30 μm size occur in the black colour of sample 2 (Fig. 8d).
33 Spot EDS analyses indicate that some aggregates are composed of manganese silicate, while
34 others are made of manganese oxide. Raman microspectrometry revealed presences of

1 braunite and hausmannite (Fig. 7b). EDS spectra indicate iron, calcium and copper as minor
2 components in the pigment particles (in sample 1: up to 5.7 wt% FeO, 1.1 wt% CaO, in
3 sample 2: up to 5.7 wt% FeO in both types of particles, in sample 6: up to 7.5 wt% FeO, 1.8
4 wt% CaO, 2.6 wt% CuO). Elevated iron content compared to the white glaze is typical for the
5 black colour (>0.7 wt%, Table 3). If applied directly over the green colour or the white glaze,
6 the black contains abundant cassiterite particles (Fig 8a, b, Table 3). The white glaze below
7 the black colour contains some manganese colorant (0.3 to 0.7 wt% MnO). If applied over the
8 yellow colour, the black does not contain cassiterite, but a few lead antimonate inclusions
9 (Fig. 8c). When applied over blue colour, the black contains some cobalt with nickel and
10 arsenic (Table 3).

11

12 4. Discussion

13 4.1 Ceramic body

14 The chemical and phase analyses indicate that the buff-coloured body of the studied
15 Anabaptist faience was produced using calcareous clay. The CaO content is in the same range
16 for the faience bodies (14.2 to 22.5 wt%) as for most of the Italian maiolica bodies (14 to 25
17 wt% CaO, Tite, 2009). Calcareous ceramic body is typical for tin-glazed pottery due to its
18 several advantages: e.g. calcareous clay fires to pale buff colour (due to the incorporation of
19 iron into high-temperature calcium silicates and aluminosilicates developed during firing), has
20 thermal coefficient matching more closely to those of lead-alkali glazes, and exhibits less
21 shrinkage during firing compared to non-calcareous clay (Molera et al., 1998, Tite et al.,
22 1998, Tite, 2009).

23 The presence of calcium silicate phases (gehlenite, diopside) formed during firing
24 indicates that the firing temperature of the faience reached 800 °C (Cultrone et al., 2001);
25 occasional presence of illite supports firing around 800 to 900 °C. Calcite detected by XRD
26 and microstructure analyses in two faience samples is a primary phase and was not
27 completely dissociated during firing due to its grain size (i.e. large calcite particles might have
28 survived firing), therefore somewhat lower firing temperature, 750 to 800 °C can be estimated
29 for these samples.

30 The absence of any significant reaction zone at the body-glaze interface suggests that
31 the body was fired to biscuit before the glaze slurry was applied (Tite et al., 1998). Biscuit
32 firing is also supported by the semi-finished products (fired, but non-glazed faience artefacts)
33 found in archaeological excavations of Hutterite ceramic workshops in Southern Moravia
34 (e.g. in Tavíkovice and Vacenovice, Pajer, 2007).

1

2 4.2 Tin glaze

3 The microchemical analyses revealed that the tin-opacified white and blue glazes covering the
4 studied Hutterite faience artefacts are of lead-alkali type. Production of such a glaze involves
5 preparation of slurry containing lead compound, alkali and silica with the addition of tin oxide
6 (Tite et al., 1998). There are several ways to prepare the glaze suspension; however, the first
7 step is the melting of lead and tin metals together to produce a mixture of lead and tin oxides
8 (lead-tin calx or calcine) as mentioned in Piccolpasso's treatise (Lightbown and Caiger-Smith,
9 2007) and in Abu'l-Qasim's treatise on Persian pottery manufacture written in 1301 (Allan,
10 1973). Alkali can be added to the glaze suspension in the form of wine lees, tartar, common
11 salt or soda. Due to its solubility in water, alkali is usually pre-fritted with silica (the latter is
12 mainly in the form of sand) before making the glaze suspension. The vitreous frit made from
13 alkali and silica is then mixed with the lead-tin calx and this mixture can be
14 (i) fritted as described in Abu'l-Qasim's treatise (Allan, 1973) or
15 (ii) not fritted, although sometimes further sand is added as in the case of the Italian maiolica
16 (Tite et al., 2008, Tite, 2009).

17 The other preparation method involves mixing the lead-tin calx directly with sand as well as
18 alkaline and other fluxes, and melting them together to vitreous frit as in the case of the 18th
19 and 19th century French faience (Maggetti, 2012). After preparation employing one of the
20 methods, the frit or the mixture is then ground to obtain a powdered raw glaze and diluted in
21 water to prepare the suspension, to which sometimes clay or other compounds are also added.

22 The angular to rounded morphology of the quartz and feldspar grains observed in the
23 tin glaze of the Hutterite faience indicates that these particles were only partially dissolved
24 during glaze firing and can be interpreted as relicts of the sand added to the glaze mixture.
25 Two generations of cassiterite crystals with different morphology and size were detected in
26 the tin glaze which can be related to the well-known phenomenon of dissolution and
27 recrystallization of the tin oxide opacifier during firing (and subsequent cooling) (Molera et
28 al., 1999; Tite et al., 2008). Angular tin oxide particles are remnants of the raw material, while
29 fine needles are *in situ* newly-formed tin oxide crystallites. Heterogeneous distribution of the
30 tin oxide particles and the partially resorbed sand grains in the Hutterite tin glaze indicate that
31 the glaze mixture (lead-tin calx + frit + sand) was not fritted when the slurry was prepared
32 before application. Therefore Hutterite potters applied similar production technique for
33 preparation of the glaze as for the tin glaze of the Italian maiolica. Mason and Tite (1997) and
34 Molera et al. (2001) supposed that the sand added to the glaze mixture, as well as the rounded

1 pores after bubbles in the glaze, contribute to the opacity of the glaze and less tin oxide is
2 needed. However, recently Tite (2009) suggested that when sand is introduced in the glaze
3 mixture the unfired, opaque glaze is more robust and less powdery and its surface is better
4 suited to taking the painted decorations. Our faience samples having a glaze with relatively
5 high tin oxide content and varying amounts of sand particles support the latter explanation.

6 The K_2O/Na_2O ratio for the Hutterite tin glaze is generally lower (0.5 to 1.0) than for
7 the maiolica glaze (1.1 to 6, Amato et al., 2010; Tite, 2009). The low ratio together with the
8 detectable chlorine (~1 wt%) indicates that a significant part of the alkali was obtained from
9 the common salt added to the frit. The tin glaze with more K_2O than Na_2O (with a ratio of
10 1.8) covers only sample 6, indicating the dominant use of K-bearing flux (wine lees, tartar).

11 The quality of faience, among other factors, depends on the quality of the tin glaze, i.e.
12 its whiteness and opacity (Vendrell et al., 2000). The whiteness of the glaze can be achieved
13 by (i) increasing its SnO_2 content, (ii) increasing its thickness and (iii) reducing the reddish
14 hue of the ceramic paste; the latter can be enhanced by using calcareous (Ca-rich) ceramic
15 pastes. Analyses of the Islamic and hispano-moresque (*múdejar*) tin-glazed pottery from
16 Spain and Italian Renaissance maiolica indicate that for production of an opaque white glaze
17 which can adequately conceal the ceramic body, the tin oxide content should be typically in
18 the range of 4-5 to 9-10 wt% with glaze thicknesses ranging from <100 μm to 600 μm (Fig. 9,
19 Molera et al., 2001; Vendrell-Saz et al., 2006; Tite, 2009). One example of the application of
20 thick tin glaze on ceramics is the Late Renaissance “bianchi” di Faenza, on which an intense
21 white glaze was produced by combining the usual tin oxide content (5.5 to 10.4 wt% SnO_2)
22 with considerable thickness (500 to 980 μm , sometimes up to 1250 μm on the front/outer side
23 of the ceramics, Tite, 2009, Amato et al., 2010). Our data indicate that the analysed
24 Anabaptist faience artefacts with buff-coloured calcareous ceramic body are covered by an
25 opaque white glaze with usual thickness, but with a significant amount of tin oxide inclusions.
26 Elevated SnO_2 content (16.9 to 20.3 wt% SnO_2) was detected compared with the Renaissance
27 maiolica: the SnO_2/PbO ratio is 0.6 to 1.8 for the Hutterite white tin glaze (Table 2), while
28 this ratio is lower (0.2 to 0.6) for most maiolica glazes (Tite, 2009). In contrast to the white
29 glaze, the Hutterite blue tin glaze contains a smaller amount of tin oxide (11 wt%) for
30 opacification, more probably due to its coloured character.

31 Very high tin oxide content (13 to 28 wt% SnO_2) with usual high lead oxide content
32 (21 to 48 wt% PbO) in glazes with 30 to 550 μm thickness was found in some of Italian
33 Archaic maiolica from the 13th and 14th centuries by Tite (2009) (Fig. 9). He explains that
34 the use of very high tin oxide content in the early period of Italian maiolica production

1 reflects a lack of understanding of the amount of tin oxide necessary to achieve adequate
2 opacity and whiteness. High tin oxide content, 14 to 20 wt% SnO₂ extending up to 24 wt%,
3 higher than the tin oxide content of Renaissance maiolica glazes, is also characteristic for the
4 white glaze of della Robbia terracotta sculptures and panels produced in the 15th and 16th
5 centuries (Fig. 9, Barbour and Olson, 2011; Gianoncelli et al., 2008; Kingery and Aronson,
6 1990; Tite, 2009; Zucchiatti et al., 2003, Zucchiatti and Bouquillon, 2011). The glaze
7 composition was deliberately modified by the della Robbia workshop to produce sculptural
8 ceramics of high artistic quality. The high presence of tin oxide in the della Robbia glazes was
9 applied in order to increase their whiteness and opacity as well as to increase their viscosity
10 which can help to compensate the decrease in viscosity due to the higher lead oxide content of
11 the glaze (up to 40 wt% PbO, Tite, 2009). It is obvious that the Hutterite potters also
12 deliberately increased the tin oxide content of the glaze and that the white glaze of faience
13 with its high tin oxide content and relatively low K₂O/Na₂O ratio resembles the della Robbia
14 glaze, the latter having a K₂O/Na₂O ratio of 0.6 to 2.5 (Tite, 2009). However, it seems that the
15 Hutterite potters did not increase the lead oxide content of the glaze, and so its moderate PbO
16 content (18 to 28 wt%) resembles that of the (Late) Renaissance maiolica glaze (Fig. 9).

17

18 4.3 Ceramic colours

19 The decorations covering the surface of the white glaze on the Anabaptist faience are
20 individual coloured glass layers. A transparent lead glaze, called *coperta*, typically covering
21 the tin glaze of many maiolica objects from the 15th century (Lightbown and Caiger-Smith,
22 2007, Tite, 2009), does not appear on the studied faience samples. The ceramic colours are
23 usually thicker, reaching several tens of µm, than the decoration layer of the *coperta*-free
24 maiolica, which is up to about 50 µm thick (Tite, 2009).

25 Ceramic colours are chemically slightly different from the white glaze. The blue,
26 green and black colours of each decorated sample have a higher total alkali content than the
27 white glaze most probably indicating the use of a different frit (glass) for these colours (e.g. in
28 sample 1 mostly 8 to 9 wt% K₂O+Na₂O in the colours vs. 6.7 wt% K₂O+Na₂O in the glaze,
29 Tables 2 and 3). However, the yellow colour has a total alkali content similar to that of the
30 white glaze on the same ceramic, indicating that a different (colourless) frit was used for the
31 yellow than for the other colours. The less than 1 K₂O/Na₂O ratio and the presence of chlorine
32 are evidences of the use of common salt in the preparation of the ceramic colours of samples
33 1 and 2, while the more than 1 K₂O/Na₂O ratio indicates the use of a higher amount of K-
34 bearing flux for the colours of sample 6.

1 Two of the ceramic colours, yellow and green, are intentionally opacified, while the
2 blue and the black are originally transparent colours. However, the latter is in several cases
3 opaque due to the fact that among the ceramic colours the black especially is greatly
4 incorporated into the underlying decorations or the white glaze during firing gaining tin oxide
5 particles as well as other colorants. In addition, the presence of a small amount of copper,
6 manganese or cobalt colorant in the white glaze under the colours suggests that diffusion
7 processes occurred between the colours and glaze during firing. These phenomena indicate
8 that the ceramic colours were applied on the surface of the unfired, powdery glaze, and then
9 the opaque glaze and colours were matured simultaneously in a single step, during the second
10 high-temperature firing, similarly to the production of maiolica. The reduced colour palette
11 (yellow, blue, green and black) of the studied Hutterite faience also supports the theory that
12 high-temperature, so-called in-glaze decorations were used.

13 The colouring and opacifying pigment for the yellow colour of the Hutterite faience
14 under study is the artificial lead antimonate. This compound is analogous with the natural
15 mineral bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$) and stable up to 1100°C (Dik et al., 2005) surviving
16 the second high temperature firing. Similar pigment was used for the yellow and orange
17 decorations of maiolica (Bultrini et al., 2006; Tite, 2009); however, lead-tin antimonate and
18 lead-zinc antimonate were also identified in some 16th century maiolica glazes by Sandalinas
19 et al. (2006) and Rosi et al. (2011). Lead antimonate was most probably produced by
20 calcinating lead oxide and antimony oxide at temperatures starting from 750°C , since instead
21 of sulphides or metals the mixture of oxides is necessary to produce lead antimonate in high
22 concentration and as purely as possible (Dik et al., 2005). The detectable Na content of the
23 pigment indicates the addition of a Na-bearing flux, i.e. NaCl, to the mixture (Dik et al.,
24 2005). Iron incorporated into the lead antimonate pigment indicates the deliberate addition of
25 iron as in the case of maiolica (Bultrini et al., 2006, Tite, 2009). Iron added to the mixture of
26 lead and antimony in the form of iron scale (rust) was also mentioned in Piccolpasso's treatise
27 (Lightbown and Caiger-Smith, 2007). Opaque colours can be produced in two ways (Maggetti
28 et al., 2009): the pigment is mixed (i) with the raw materials of the glass, then fired, and after
29 cooling the opaque glass is powdered, or (ii) with the already prepared, powdered, transparent
30 (or coloured) glass. The use of the later preparation method is indicated by the presence of the
31 angular and sometimes clustered lead antimonate particles as well as the quartz and feldspar
32 particles, the latter being relicts of the additional sand added to the glaze suspension. The low
33 antimony, but higher iron content of the vitreous matrix of the yellow colour probably
34 indicates that the reaction of lead antimonate particles with the glass was limited.

1 The green decoration of the faience is opaque due to the addition of tin oxide to the
2 glass; however, smaller amounts of tin oxide were used for opacification than for the white
3 glaze. The green glassy decoration was coloured with copper colorant. Piccolpasso described
4 in his treatise two types of green pigment: (i) “burnt copper” (*ramina*), which is copper oxide
5 prepared by burning (oxidising) copper metal and its colour in lead-alkali glazes is green with
6 bluish tint, and (ii) “mixed green”, which is a prefired mixture of copper oxide, lead oxide and
7 antimony oxide and its colour is green without any bluish tint (Lightbown and Caiger-Smith,
8 2007, Tite, 2009). Copper dissolved in the glassy matrix in combination of abundant lead
9 antimonate particles was observed for della Robbia green glaze (Tite, 2009). Lead antimonate
10 particles only very sporadically occur in the green glaze of the faience under study, therefore
11 “burnt copper” was used for colouring, similarly to the Archaic and medieval green maiolica
12 glazes (e.g. Ricci et al., 2005).

13 The cobalt colorant associated with nickel, arsenic and small amounts of iron in the
14 blue colour as well as in the blue tin glaze of the Anabaptist faience indicates the use of a
15 pigment made of impure cobalt oxide prepared by roasting arsenic-bearing cobalt-nickel ore
16 minerals like arsenides, arsenosulphides or arsenates. In the blue glaze of terracotta sculptures
17 arsenic appears around 1520, whereas arsenic is absent (i.e. below detection limit, <0.1 wt%
18 As₂O₃ for PIXE) in blue glaze produced before 1520 (Padeletti et al., 2006; Pappalardo et al.,
19 2004; Zucchiatti et al., 2006). The arsenic content of the pigment is separated from the cobalt
20 and typically present in the form of newly-formed calcium-lead arsenate crystals in the
21 vitreous matrix (e.g. Viti et al., 2003; Zucchiatti et al., 2006) as in the blue decorations of the
22 16th century *berettino* ceramics from Faenza (Tite, 2009). The same arsenate particles were
23 also detected in the blue colour and the blue tin glaze of the studied faience artefacts. Based
24 on the analysis of blue glasses and ceramic glazes Gratuze et al. (1996) suggested that the
25 most probable source of cobalt pigment used by glassmakers and potters from the 13th to the
26 18th century is the Erzgebirge region of Saxony and Bohemia. In the Erzgebirge region the
27 ‘five-element’ (Ni-Co-As-Ag-Bi(-U)) veins were exploited (Kissin, 1992). Two cobalt
28 pigments were produced in this region: (i) *zaffre* (*safre*, *zaffer*, *zaffera*), invented around
29 1520, which is a roasted Co-Ni-Fe-As ore, that is, an impure cobalt oxide with a presence of
30 arsenic due to incomplete roasting (Padeletti et al., 2004, Barilaro et al., 2008) and/or partial
31 recuperation during processing (Zucchiatti et al., 2006) and (ii) *smalt* (*smalte*), invented
32 around 1540-60, which is a potassium glass obtained by melting the roasted cobalt ore
33 together with quartz (sand) and potash or added to molten glass (Mühlethaler and Thissen,
34 1969). Pigments characterised by Co-As-Ni-Bi(-Fe) element association from the Erzgebirge

1 region were used from the 15th to the 18th century (Gratuze et al., 1996). We suppose that
2 Anabaptists might also have imported cobalt pigment from this region. The absence of
3 discrete cobalt pigment particles in the blue colour of the studied faience artefacts indicates
4 the use of smalt rather than zaffre.

5 In the black decoration of the Hutterite faience we detected manganese accompanied
6 by minor iron. Manganese was used for colouring purple and brown decorations of maiolica
7 (e.g. for Archaic maiolica, Alaimo et al., 2004; Ricci et al., 2005); however, in addition to
8 manganese and iron, the presence of cobalt, nickel, copper and antimony indicating complex
9 mixing of colours to produce black was detected in some della Robbia and maiolica glazes as
10 well (Padelletti et al., 2006; Zucchiatti and Bouquillon, 2011). Manganese oxides, mostly
11 pyrolusite (Mn^{4+}O_2) as well as manganese-iron nodules and concretions composed of several
12 oxides and oxihydroxides of manganese and iron might have been used as pigments (Alaimo
13 et al., 2004).

14 In the black colour discrete manganese-bearing particles occur: braunite (manganese
15 oxysilicate, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$) and hausmannite (manganese oxide, $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$). Similar
16 compounds were also detected in the purple-brown-black decorations of Spanish tin-glazed
17 ceramics, Italian maiolica (Molera et al., 2013; Pradell et al., 2013), and Portuguese tiles
18 (Coentro et al., 2012), and interpreted as newly-formed crystals or pigment remnants. The
19 idiomorphic morphology of crystals in the black colour of two Anabaptist faience artefacts
20 (samples 1 and 6) clearly indicate that the braunite was crystallized *in situ* during firing (and
21 subsequent cooling). In one of the studied faience artefacts (sample 2) the pigment particles
22 preserved the original morphology of the manganese pigment, but after firing their
23 mineralogical composition became that of braunite and hausmannite. In the black ceramic
24 colour, as temperature increased the Mn^{4+}O_2 (pyrolusite) pigment started to decompose
25 (deoxidise) in air at about 550-600 °C to $(\text{Mn}^{3+},\text{Fe}^{3+})_2\text{O}_3$ (bixbyite), and at about 870-900 °C,
26 or a higher temperature depending also on the iron oxide content, to $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$
27 (hausmannite) (Dent Glasser and Smith, 1968; Muan, 1959; Muan and Somiya, 1962; Roy,
28 1968). In this case a reaction with the silica-rich molten glaze is responsible for the formation
29 of braunite as suggested by Molera et al. (2013) and Pradell et al. (2013). Considering the
30 phase equilibria in the system manganese oxide-SiO₂ in air, braunite can be stable at
31 temperatures up to 1168 °C depending on the silica content of the system (Muan, 1959).

32

33 5. Conclusions

1 In comparing the 17th century Anabaptist (Hutterite) faience artefacts from NE Hungary
2 under study with their direct or indirect precursor, Italian Renaissance maiolica, similarities as
3 well as differences are observed between the production technologies of the two tin-glazed
4 ceramics.

5 Similarities:

- 6 (i) use of calcareous clay for the ceramic body, which was biscuit-fired,
7 (ii) use of tin-opacified lead-alkali glaze, where the glaze suspension contained an admixture
8 of sand and significant amount of common salt, and was not fritted before application,
9 (iii) use of similar colorants for ceramic colours: lead antimonate for yellow, cobalt with
10 arsenic, nickel and iron for blue, copper for green, manganese with iron for black; decorations
11 were applied on unfired opaque glaze and matured during the second firing.

12 Differences:

- 13 (i) higher amount of tin oxide added to the white glaze,
14 (ii) no application of outer transparent glaze (*coperta*), use of ceramic colours comparable in
15 thickness with the opaque glaze.

16 The most important difference is the tin oxide content, which is definitely higher (17
17 to 20 wt% SnO₂) in the white glaze of the studied Hutterite faience artefacts compared to that
18 of the white glaze of the Renaissance maiolica, and reaches the elevated tin oxide content
19 typical for the white glaze of della Robbia terracotta. A high amount of tin oxide was
20 deliberately used by the Hutterite potters to produce high-quality white glaze instead of
21 increasing its thickness.

22

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23 Table and figure captions

24

25 Table 1. Chemical composition (in wt%) of the ceramic body of the studied Hutterite faience
26 artefacts (average of area measurements for 'bulk' composition by EDS, standard deviation in
27 parenthesis, n: number of analyses, results are normalised to 100%, original analytical totals
28 are also indicated).

29

30 Table 2. Chemical composition (in wt%) of the white and blue tin glaze of the studied
31 Hutterite faience artefacts (average of area measurements for 'bulk' composition and spot
32 measurements for matrix composition by EDS, standard deviation in parenthesis, n: number
33 of analyses, results are normalised to 100%, original totals are also indicated, na: not
34 analysed).

1

2 Table 3. Chemical composition (in wt%) of the ceramic colours of the studied Hutterite
3 faience artefacts (average of area measurements for 'bulk' composition and spot
4 measurements for matrix composition by EDS, standard deviation in parenthesis, n: number
5 of analyses, results are normalised to 100%, original totals are also indicated, na: not
6 analysed).

7

8 Fig. 1. Location of Sárospatak in Hungary.

9

10 Fig. 2. The studied Hutterite faience artefacts, (a) sample 1: fragment of a jug, (b) sample 2:
11 fragments of a bowl, (c) sample 3: fragments of a bowl, (d) sample 4: fragments of a bowl, (e)
12 sample 5: fragment of a bowl?, (f) sample 6: fragment of a tazza, the inset shows it from the
13 lateral view.

14

15 Fig. 3. (a) X-ray diffraction patterns of the ceramic body of the studied samples (st: standard,
16 SnO₂ derives from the tin glaze). BSE images showing the microstructure of the ceramic body
17 of sample 1 (b) with a void due to dissociation of carbonate and (c) with a non-dissociated
18 (residual) carbonate (calcite). Q: quartz, M: matrix, CC: calcite, V: void (tiny bright crystals
19 on fig. a are Pb±Sb particles).

20

21 Fig. 4. The microstructure and inclusions of the tin glaze (BSE images). (a) white tin glaze
22 with high concentration of tin oxide (bright inclusions) and quartz and feldspar particles (dark
23 inclusions) (sample 4), (b) tin oxide (abbreviated as cass) particles and aggregates of needles
24 in white tin glaze (sample 1), (c) blue tin glaze with tin oxide and small amount of quartz and
25 feldspar particles (sample 6), (d) calcium-lead arsenate needles and prisms in a rounded pore
26 in the blue tin glaze (sample 6).

27

28 Fig. 5. Yellow, blue and black colours over white glaze (sample 2, BSE image).

29

30 Fig. 6. The microstructure and inclusions of the colours (BSE images). (a) bright lead
31 antimonate particles and aggregates and dark quartz particles in the yellow colour over white
32 glaze (sample 1), (b) bright lead antimonate and dark quartz particles in the yellow colour
33 (sample 2), (c) blue colour over white glaze (sample 1), (d) tiny, bright arsenate crystals and
34 dark quartz and silica particles in the blue colour (sample 2).

1

2 Fig. 7. Raman spectra of the colour pigments. (a) lead antimonate identified in yellow colour
3 of (i) sample 1 and (ii) sample 2, (b) braunite identified in the black colour of (i) sample 1, (ii)
4 sample 2, (iii) sample 6 and (iv) the reference spectrum of braunite from the RRUFF database
5 (R050385); (v) hausmannite identified in sample 2 and (vi) the reference spectrum of
6 hausmannite from the RRUFF database (R060512).

7

8 Fig. 8. The microstructure and inclusions of the colours (BSE images). (a) green and black
9 colours over white glaze (sample 6), (b) idiomorphic manganese silicate (braunite, br) crystals
10 in the black colour (sample 6), (c) idiomorphic manganese silicate (braunite, br) crystals in
11 the black colour over yellow colour (sample 1), (d) manganese pigment particles in the black
12 colour: hausmannite (h) and braunite (br) (sample 2).

13

14 Fig. 9. Variation diagram PbO vs. SnO₂ for the white glaze of the studied Hutterite faience
15 artefacts (see Table 2) compared with the white glaze of the Archaic, Early and Late
16 Renaissance Italian maiolica (data from Viti et al., 2003, Tite, 2009, Amato et al., 2010) and
17 white glaze of della Robbia sculptural ceramics (data from Kingery and Aronson, 1990,
18 Zucchiatti et al., 2003, Gianoncelli et al., 2008, Tite, 2009, Barbour and Olson, 2011). The
19 chemical compositions as measured by SEM-EDS analyses for maiolica glaze, and SEM-
20 EDS, microprobe and portable XRF analyses for della Robbia glaze, respectively.
21 Explanations: ●: studied Hutterite faience, ▲: Archaic maiolica, ◆: Early Renaissance
22 maiolica, ◇: Late Renaissance maiolica, ■: della Robbia terracotta.

Table 1

Sample	n	SiO₂	Al₂O₃	Na₂O	K₂O	MgO	CaO	TiO₂	FeO	Orig. total
sample 1	3	53.14 (3.22)	13.80 (0.62)	1.04 (0.36)	2.27 (0.29)	2.99 (0.22)	21.23 (1.59)	0.63 (0.19)	4.91 (0.34)	71.89 (4.21)
sample 2	3	53.63 (1.20)	12.77 (0.66)	1.03 (0.40)	2.20 (0.35)	2.85 (0.32)	22.46 (0.77)	0.44 (0.06)	4.62 (0.28)	69.76 (3.11)
sample 3	3	55.08 (1.06)	16.50 (0.59)	1.36 (0.15)	2.68 (0.10)	3.77 (0.25)	14.51 (0.43)	0.70 (0.07)	5.40 (0.41)	73.35 (5.26)
sample 4	4	57.61 (1.02)	15.04 (0.62)	1.26 (0.29)	2.70 (0.13)	2.93 (0.17)	15.99 (0.70)	0.58 (0.07)	3.91 (0.19)	71.87 (4.51)
sample 5	4	56.05 (0.22)	15.84 (0.31)	1.33 (0.14)	2.75 (0.27)	4.11 (0.26)	14.16 (0.37)	0.68 (0.08)	5.08 (0.27)	74.88 (0.63)
sample 6	6	54.58 (1.27)	16.32 (0.98)	0.78 (0.13)	2.50 (0.25)	2.82 (0.28)	17.91 (0.45)	0.62 (0.11)	4.48 (0.15)	72.10 (2.57)

Table 2

Sample	n	SiO ₂	PbO	SnO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	FeO	CoO	NiO	As ₂ O ₃	Cl	Orig. total	SnO ₂ /PbO	K ₂ O/Na ₂ O	K ₂ O+Na ₂ O	
Tin-opacified white glaze																			
Sample 1	Bulk	4	46.33 (1.09)	23.14 (2.34)	20.34 (0.73)	4.15 (1.00)	2.58 (0.55)	1.04 (0.31)	0.12 (0.15)	1.27 (0.22)	0.34 (0.12)	na	na	na	0.69 (0.14)	98.40 (3.29)	0.88	0.62	6.73
	Matrix	24	55.21 (2.84)	28.66 (4.53)	5.48 (2.08)	3.09 (0.76)	3.15 (0.42)	1.67 (0.92)	0.12 (0.23)	1.26 (0.65)	0.44 (0.70)	na	na	na	0.91 (0.30)	99.00 (2.43)			
Sample 2	Bulk	8	44.06 (0.36)	26.49 (0.73)	16.87 (0.66)	3.70 (0.46)	3.68 (0.29)	1.34 (0.44)	0.13 (0.11)	2.50 (0.36)	0.18 (0.19)	na	na	na	1.05 (0.19)	94.79 (1.13)	0.64	0.99	7.38
	Matrix	28	52.55 (1.87)	31.90 (3.17)	4.18 (0.85)	2.54 (0.51)	3.77 (0.41)	1.63 (0.95)	0.15 (0.27)	2.04 (0.57)	0.15 (0.23)	na	na	na	1.09 (0.26)	97.06 (2.72)			
Sample 3	Bulk	5	43.41 (1.86)	27.69 (1.30)	19.30 (0.96)	3.79 (0.13)	2.02 (0.16)	0.58 (0.17)	0.03 (0.13)	2.12 (0.24)	0.20 (0.17)	na	na	na	0.87 (0.04)	94.30 (4.37)	0.70	0.53	5.81
	Matrix	7	51.26 (0.83)	36.73 (1.16)	2.80 (0.78)	2.20 (0.31)	2.44 (0.36)	0.75 (0.10)	0.08 (0.15)	2.40 (0.36)	0.15 (0.25)	na	na	na	1.19 (0.19)	94.50 (2.36)			
Sample 4	Bulk	3	49.53 (0.53)	17.88 (1.14)	20.21 (1.60)	2.89 (0.24)	2.94 (0.15)	2.41 (1.17)	0.27 (0.11)	3.10 (0.45)	0.38 (0.18)	na	na	na	0.39 (0.07)	95.01 (3.18)	1.13	1.02	5.83
	Matrix	22	54.46 (1.69)	26.68 (2.53)	6.09 (1.86)	3.00 (0.50)	3.89 (0.52)	2.17 (0.61)	0.18 (0.18)	2.55 (1.02)	0.32 (0.20)	na	na	na	0.68 (0.16)	99.44 (2.83)			
Sample 5	Bulk	3	44.63 (0.38)	26.22 (0.95)	19.27 (1.15)	3.26 (0.23)	2.50 (0.39)	0.85 (0.16)	0.07 (0.08)	2.19 (0.40)	0.11 (0.16)	na	na	na	0.88 (0.09)	94.27 (1.42)	0.73	0.77	5.77
	Matrix	19	52.74 (2.04)	32.49 (2.51)	3.85 (0.72)	2.60 (0.43)	3.28 (0.37)	1.17 (0.66)	0.09 (0.19)	2.22 (0.32)	0.24 (0.21)	na	na	na	1.31 (1.09)	97.92 (2.69)			
Sample 6*	Bulk	3	48.57 (2.16)	22.05 (0.86)	17.10 (0.84)	2.54 (0.09)	4.47 (0.28)	1.08 (0.20)	0.18 (0.16)	2.32 (0.09)	0.31 (0.11)	0.15 (0.07)	-0.03 (0.24)	0.23 (0.19)	1.02 (0.11)	96.18 (2.87)	0.78	1.76	7.02
	Matrix	18	56.96 (2.30)	25.78 (3.53)	4.13 (1.59)	1.77 (0.45)	5.03 (0.63)	1.56 (0.67)	0.21 (0.22)	2.77 (1.19)	0.46 (0.31)	0.13 (0.25)	-0.03 (0.26)	0.20 (0.15)	1.15 (0.77)	96.01 (4.40)			
Tin-opacified blue glaze																			
Sample 6	Bulk	9	46.50 (0.93)	28.10 (0.71)	11.06 (1.44)	3.07 (0.30)	4.94 (0.38)	0.85 (0.17)	0.04 (0.13)	1.94 (0.38)	0.74 (0.24)	0.68 (0.26)	0.16 (0.10)	0.86 (0.12)	1.06 (0.08)	97.76 (2.35)	0.39	1.61	8.02
	Matrix	57	53.07 (2.17)	30.65 (2.77)	2.76 (0.96)	2.03 (0.40)	4.55 (0.57)	1.29 (0.68)	0.20 (0.23)	1.57 (0.72)	0.98 (0.41)	0.80 (0.24)	0.17 (0.29)	0.78 (0.38)	1.15 (0.91)	98.91 (4.00)			

*white glaze partly below blue colour

Table 3

Sample		n	SiO ₂	PbO	SnO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	FeO	CoO	NiO	As ₂ O ₃	Sb ₂ O ₃	CuO	MnO	Cl	Orig. total	K ₂ O/ Na ₂ O	K ₂ O+ Na ₂ O
Yellow																					
Sample 1	Bulk	3	43.66 (1.26)	37.01 (1.35)	0.34 (0.33)	4.00 (0.48)	2.53 (0.21)	0.71 (0.02)	0.20 (0.02)	2.95 (0.43)	2.08 (0.07)	na	na	na	6.11 (1.08)	na	na	0.41 (0.14)	96.53 (3.03)	0.63	6.53
	Matrix	9	51.73 (1.16)	35.23 (1.65)	0.37 (0.53)	2.24 (0.34)	2.75 (0.30)	0.35 (0.13)	0.19 (0.14)	3.38 (0.85)	2.10 (0.34)	na	na	na	1.16 (0.67)	na	na	0.50 (0.24)	96.09 (1.89)		
Sample 2	Bulk	4	50.09 (2.06)	25.49 (1.22)	0.86 (0.66)	3.59 (0.31)	3.43 (0.41)	0.75 (0.10)	0.23 (0.13)	3.41 (0.30)	2.81 (0.41)	na	na	na	8.87 (0.44)	na	na	0.47 (0.15)	95.02 (1.93)	0.96	7.03
	Matrix	10	58.36 (2.39)	25.10 (1.48)	0.33 (0.43)	1.91 (0.43)	3.39 (0.46)	0.35 (0.10)	0.29 (0.18)	3.00 (0.81)	3.87 (1.20)	na	na	na	0.33 (0.43)	na	na	0.48 (0.24)	96.22 (1.93)		
Blue																					
Sample 1	Bulk	3	51.40 (0.26)	31.95 (1.01)	2.01 (0.31)	5.39 (0.80)	3.57 (0.21)	0.96 (0.08)	0.05 (0.02)	1.19 (0.07)	1.12 (0.14)	0.77 (0.21)	0.48 (0.04)	0.71 (0.32)	na	na	na	0.39 (0.09)	92.77 (5.54)	0.66	8.96
Sample 2	Bulk	2	56.06	25.69	1.20	4.80	3.61	0.81	0.11	1.57	1.40	1.10	0.95	1.62	na	na	na	1.08	92.23	0.75	8.41
Sample 6	Bulk	2	47.96	33.40	3.51	3.40	4.81	0.70	-0.13	0.80	1.42	1.38	0.34	1.71	na	na	na	0.69	94.74	1.42	8.21
Green																					
Sample 1	Bulk	4	40.49 (0.83)	30.82 (0.67)	13.78 (0.54)	5.44 (0.07)	2.56 (0.04)	0.85 (0.10)	0.26 (0.10)	2.39 (0.30)	0.61 (0.17)	na	na	na	0.20 (0.43)	1.82 (0.17)	na	0.77 (0.06)	96.55 (0.86)	0.47	8.00
	Matrix	8	47.78 (1.16)	36.18 (0.99)	3.05 (0.41)	3.09 (1.19)	2.59 (0.22)	0.85 (0.24)	0.27 (0.13)	2.65 (0.54)	0.60 (0.22)	na	na	na	na	2.02 (0.36)	na	0.91 (0.26)	90.44 (1.58)		
Sample 6	Bulk	6	47.81 (1.48)	24.47 (2.64)	10.97 (1.92)	3.75 (0.31)	5.15 (0.36)	0.91 (0.09)	0.38 (0.12)	3.94 (1.04)	1.16 (0.44)	na	na	na	na	0.66 (0.22)	na	0.81 (0.17)	98.37 (1.72)	1.37	8.89
	Matrix	9	53.16 (1.43)	30.01 (2.17)	3.48 (1.74)	2.12 (0.22)	4.18 (0.35)	1.26 (0.26)	0.35 (0.12)	2.17 (1.00)	0.94 (0.59)	na	na	na	na	1.19 (0.27)	na	1.13 (0.26)	95.43 (1.93)		
Black																					
Sample 1*	Bulk	1	38.83	24.46	16.75	5.25	2.94	1.51	0.38	2.48	1.30	na	na	na	na	0.33	5.36	0.42	87.89	0.56	8.19
	Matrix	2	48.89	28.06	4.23	2.88	3.29	1.94	0.35	2.76	1.12	na	na	na	na	0.56	5.40	0.51	88.48		
Sample 1**	Bulk	1	38.29	21.62	0.68	4.88	2.14	1.28	0.59	2.50	3.20	na	na	na	na	na	24.61	0.20	91.13	0.44	7.02
	Matrix	2	48.01	31.48	0.50	3.41	3.15	1.47	0.28	3.61	2.57	na	na	na	na	na	5.35	0.17	92.12		
Sample 2***	Bulk	1	41.30	33.84	6.74	5.05	3.73	0.73	0.19	2.62	0.71	na	na	na	na	na	4.05	1.05	100.33	0.74	8.78
	Matrix	3	46.58 (1.47)	34.65 (2.52)	2.78 (1.13)	3.00 (1.53)	3.84 (0.35)	0.59 (0.01)	0.40 (0.16)	2.32 (0.33)	0.78 (0.18)	na	na	na	na	na	4.22 (0.25)	0.85 (0.13)	96.42 (0.85)		
Sample 2**	Bulk	3	42.54 (3.07)	25.67 (0.59)	1.63 (0.22)	5.61 (0.26)	3.15 (0.36)	0.70 (0.12)	0.04 (0.14)	2.81 (0.24)	1.45 (0.17)	0.89 (0.08)	0.72 (0.17)	1.52 (0.31)	na	na	12.49 (4.44)	0.78 (0.10)	95.16 (1.35)	0.56	8.76
	Matrix	4	48.81 (1.73)	30.30 (1.71)	0.29 (0.93)	2.32 (0.31)	2.91 (0.18)	0.80 (0.13)	0.25 (0.12)	3.88 (0.96)	1.51 (0.08)	0.70 (0.41)	0.50 (0.36)	1.33 (0.28)	na	na	5.64 (0.43)	0.76 (0.24)	92.36 (1.25)		
Sample 6*	Bulk	4	44.91 (1.70)	23.63 (1.61)	12.24 (1.58)	4.11 (0.68)	4.87 (0.51)	1.14 (0.28)	0.24 (0.21)	3.58 (0.82)	1.11 (0.23)	na	na	0.13 (0.26)	na	0.63 (0.35)	2.53 (1.36)	0.89 (0.24)	96.03 (2.92)	1.18	8.98
	Matrix	13	50.44 (2.63)	28.22 (1.81)	2.12 (0.82)	2.36 (0.29)	4.60 (0.39)	1.56 (0.32)	0.28 (0.18)	3.27 (0.69)	1.41 (0.42)	na	na	0.42 (0.50)	na	0.76 (0.39)	3.77 (1.38)	0.80 (0.28)	95.12 (1.94)		

* black colour over green colour, ** black colour over yellow (sample 1) or blue colour (sample 2), *** black colour over white glaze,

















