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Original Article

On-site pXRF analysis of body, glaze and colouring agents of the tiles at the excavation site of Iznik kilns

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ABSTRACT

The excavation at Iznik tiles kilns continues as the third period of the field mission. We present here the first on-site, non-invasive analyses performed with portable XRF instrument on twenty-five excavated tiles and two residue materials of the kiln. The shards studied were attributed to the productions from 14th- to 17th-centuries. The comparison was made by the discussion of characteristic elemental ratios selected from the ceramic technology criteria and PCA/Euclidean distances analysis. Three groups of body and glaze technologies were evidenced. We encountered that the amount of tin oxide in the glaze decreased over the centuries. Besides, two different types of fluxes were used in the glaze, some containing only potassium, and the others having potassium and calcium. The decors, which were investigated in this study were blue, turquoise, green, red colours, and black lines. A copper-iron mixture in the red areas was documented, which reflects the use of bornite.

1. Introduction

The excavations in Iznik, which aim to present the history and cultural heritage of the city, started in 1969 in the sites of Orhan Imaret and its Bath (Turkish Hamam) and continued for kilns [1]. Since 4th-century BC, Iznik, known as Nicaea under Byzantium rule, has been located in Anatolia at the intersection of the roads linking the Middle-East region to the Balkan states [2]. Iznik came into prominence when the ceramic production had developed during the Ottoman Empire. The excavation work of Iznik tiles kilns continues as the third period of the field mission [3]. The origin of Iznik technology remains debated because the links with the know-how of Seljuk, Timurid, and Byzantine productions of Nicaea are not well defined due to the limited studies carried out at the excavation site and on the ancient Ottoman buildings historically well documented. Most of the holy places, mosques, and similar architecture built in Istanbul, Edirne, and Bursa were ornamented with the "Iznik" style tiles [4–10]. Indeed, Ottoman sources state that the Iznik production was used more as a trade name than a provenance [11]. This study aims to identify the technology of tiles produced in the kilns of Iznik city and define the technological links between Timurid and Seljuk productions.

Since the 1980s, mostly laboratory studies with large-scale, destructive/invasive instruments and few on-site measurements with some portable, non-invasive techniques were conducted about the characterization of Ottoman period ceramics, where the research on Iznik and Kütahya productions lead, by international [12–20] and national researchers [21–25]. Mainly, the material studied on-site concerns the collections of the museums [19,20], and rarely on buildings [25]. The place or places of the production of "Iznik" style ceramics are still debated, the number of shards found in the excavation context is reduced and the measurements have been focused more on the analysis of paste and mostly published in an inaccessible form for international researchers due to the national language used [1,11,27,28]. The analyses concerning the colouring agents are old and limited to a few fragments whose origin is poorly or not documented. The most comprehensive work comprises the analyses of the shards preserved in the vaults of the Topkapi Palace Museum with scanning electron microscopy-energy dispersive spectrometer (SEM-EDS) and Raman instruments [11,26,27]. The aim was to characterize non-inventoried shards and attribute the productions of Iznik, Kütahya, Tekfur Palace (Istanbul), and some other Ottoman ceramics of unknown origin by comparing the microstructure of the cross sections, glaze signatures and chemical composition of the bodies, glazes, and pigments found in the coloured areas.

On the contrary to the analyses of movable and immovable cultural assets of Iznik production, very few works were conducted on the

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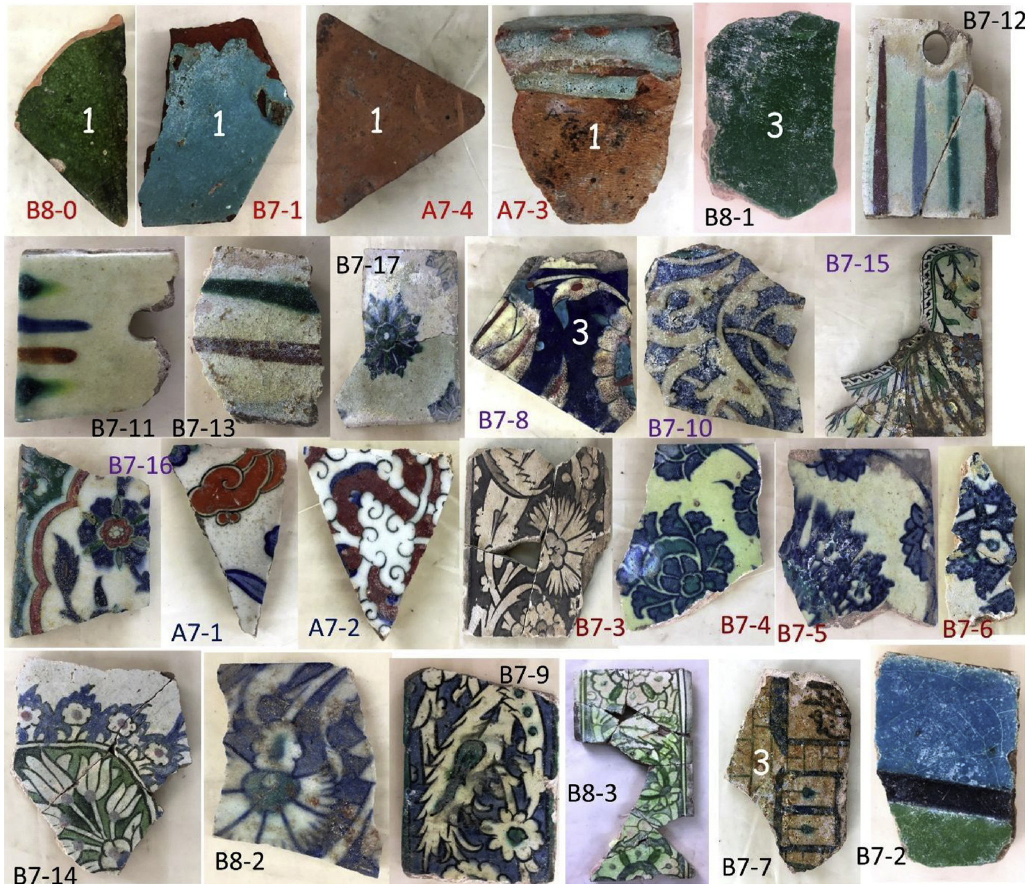


Fig. 1. On-site studied shards excavated from the Iznik Tile Kilns (Turkey) which were attributed to the productions from 14th- to 17th-centuries; see Table S1 for details. The number 1 represents the shards having clayey body, and 3, calcareous body. The rest belongs to the group 2 which represents stonepaste tiles.

excavation materials of the Iznik tile kilns and the studies were performed only with destructive techniques [2,28–30]. During her Ph.D. work, Füsun Okyar [28] performed petrographic and chemical analyses of the bodies, slips, glazes, and coloured decors of the shards of redware and stone-paste type, on twenty-four samples in total. Chemical compositions were defined with SEM-EDS method. The research on the excavation materials continued with the studies of T. Tulun and her colleagues by using similar techniques (e.g. XRD, SEM-EDS) to identify the technological properties [2]. In this study, the results obtained by F. Okyar [28] and T. Tulun [2] are used as references to compare the data obtained with pXRF.

The advantage of the use of laboratory-type instruments is the possibility of a multi-scale analysis of the sections (including glaze, decor, slip, and body) of the shards. The high-resolution techniques, including petrographic microscopy, SEM-EDS, micro-XRD (X-rays diffraction), micro-XRF (X-rays fluorescence), and micro-Raman, with high detection capabilities, are the best approaches to understand the differences and common points in the ceramic production technologies. Due to the destructive character of the techniques, ethical rules of cultural heritage studies now limit these types of analyses as much as possible. Moreover, the shards from Iznik kilns are rare and the research ethic, especially in Turkey, covers the use of non-destructive techniques to maintain the integrity of the samples. Due to the complexity of the Iznik decors with superposition of several layers of enamels, the analysis by micro-techniques imposes one of the cuts incompatibles with the respect of the artifacts. In addition, most of the documented “Iznik” tiles are in UNESCO World Heritage sites and their analysis can only be performed by non-invasive methods. Therefore, the portable, non-destructive techniques, e.g., pXRF, pRaman, and FORS (Fiber Optics Reflectance (UV-nIR) Spectroscopy) have become essential tools for the analyses of the objects in place (tiles) or exclusive objects preserved in the secure rooms of museums or private collections. Thus, a methodology must be created to make the analytical procedures more reliable when using portable instruments.

Moreover, the main drawback of studying the excavation materials is the interpretation of the results regarding the production technology. The materials found at the excavation site could be trials of the artist to define the best recipe for the artwork he/she prepared or some rejected ceramics due to the inappropriate temperature and atmosphere control of the kiln or wrong choice of the raw materials for the body and glaze. However, the tile shards found inside the kiln are in general statistical representatives of the production and can be compared with the tiles found in the wall revetments of the buildings. The portable instruments, which allow non-invasive and fast measurements, help to analyse a huge number of artefacts leading a statistical approach which compares the tiles of the excavation sites with the tiles mounted on the walls of the buildings of similar periods. In addition, a few tiles can be extracted to be cut and prepared for destructive methods at the laboratory, which will provide individual data rather than a cumulative knowledge. Therefore, portable, non-destructive techniques are gaining in importance. Thus, defining the provenance of the collections will be supported by investigating the excavation materials.

This study presents the characterization of twenty-five shards excavated recently and two residue materials formed on the walls in the Iznik tile kilns. The work has two objectives: i) the comparison of elementary data analysis based on the comparison of the elemental ratio, which is characteristic of the ceramic technology, with the ‘blind’ approach using PCA and Euclidian dendrograms; ii) a better knowledge of the production of Iznik kilns. Moreover, the results of pXRF measurements will correlate the previous measurements carried out on the excavation materials with large-scale laboratory-type instruments in order to assess the capabilities of the portable XRF system.

2. Experimental

2.1. Tile shards

Twenty-three glazed shards and two shards not glazed but one painted and the other non-painted, were examined with the pXRF instrument in this study in addition to the measurement of kilns residues on-site and in the excavation lab. Fig. 1 shows all the studied shards which were excavated from the tile kilns in Iznik. The shards, which were shown on the first three lines, were attributed to the productions of 14th-16th centuries and shards on the last line are assumed to be later productions of the 17th-century. In addition to the ceramic fragments, one fall-out material (see Fig. S1), which were formed on the walls inside the kiln, was measured with pXRF. The detailed information about the tiles studied is given in Table S1. The dating of the shards was determined aesthetically by the director and sub-director of Iznik tiles kilns excavations related to the building, where similar types of tiles were used [32–34]. In contrast to tableware production, tiles were always produced by order of the Sultans to be used as wall decorations, in the architectural buildings, holy places, mosques, etc. Therefore, the production date of the tiles is much better documented compared with the tableware ceramics. Furthermore, the aesthetical and technical characteristics of the tiles change through the centuries. Ottoman ceramic art technology started with both coloured glaze and underglaze decor but with changing the quality of the body and glaze composition, and colours in the decors. With the regression of the refined structure of Iznik ceramics from 17th-century, poorer quality of paste and glaze [9,10,17,19,35], decorated with coarse patterns are seen on the tiles which were produced for e.g., Blue Mosque, Valide Sultan Mosque (Eminönü, Istanbul). Additionally, the dating of the tiles was determined depending on the restoration records of the buildings [1,34].

Out of the intact tiles, one fall-out material (F1) of the unattributed period (15th-, 16th- or 17th-c.), which was formed on the walls of the kiln, is measured with pXRF. Besides, one measurement at the excavation site was performed on the external surface of the kiln walls in order to identify the chemical composition of the green formation (see Fig. S2).

Among the tiles of 14th and 16th-centuries (Fig. 1), four of them (B8-0, B7-1, A7-3, B8-1) have monochrome glazes and red bodies rather similar to the hexagonal tiles of Yeşil Cami (Bursa, 1424–1429), Muradiye Cami (Bursa, 1426), Muradiye Cami (Edirne, 1435–1436), and Şah Melek Paşa Cami (Edirne, 1429). These shards are thicker than the others, like a brick. Additionally, another shard in triangle form (A7-4), which is assumed to be included in the same group is fired once, unglazed, and not painted (biscuit form). Three tiles (B7-11, B7-12, B7-13) of the group seem to be prototypes, where the artisan may have been trying to determine different hues of the primary colours (blue, red, and green). Six shards (B7-8, B7-10, B7-15, B7-16, A7-1, A7-2) belong to the group of the classical, polychrome “Iznik” tiles as observed in Süleymaniye Cami (Istanbul, 1557), Kanuni Sultan Türbesi (Istanbul, 1566), Selimiye Cami (Edirne, 1569-75), and Sultan II. Selim Türbesi (Istanbul, 1576-77). The last five tiles (B7-4, B7-5, B7-6, B7-17, and B7-3) of this group are painted in triple colours (blue-white-turquoise), just one being unglazed but already decorated. B7-3 is an example representing the technology of underglaze painting.

The 17th-century tiles include two shards (B8-2, B7-9) with underglaze decoration in three colours (blue-white-turquoise) as observed in the sunnah room of Topkapi Palace (Istanbul, restoration in 17th century), Sultan Ahmet Türbesi (Istanbul, 1620), and Pavilion Revan in Topkapi Palace (Istanbul, 1638). The other shard (B7-2) was also decorated in triple coloured glaze being turquoise, green and dark blue thick contour. Three of them (B7-14, B8-3, and B7-7) are polychromic, one decorated with the pattern of Kaaba. F1 is a fall-out material, which was formed on the wall of the kiln as a brown glaze layer. In the case of lead-rich glazes, when the firing temperature is above 850 °C, lead oxide (PbO) vapour starts to deposit on the walls of the kiln since it is quite volatile.

2.2. Technique

Elemental, semi-quantitative measurements were carried out non-destructively with a hand-held X-Ray Fluorescence spectrometer positioning the Hitachi X-MET 8000 Expert Geo (Oxford Instruments) in contact with the tiles. The instrument was equipped with a rhodium (Rh) target X-ray tube of 4 W, 50 kV max and a silicon drift detector (SDD). It was operated by using the Mining LE method, in which two shots were performed, one at the lower energy (10 keV) for determining low Z elements (Mg and higher Z number) essentially for the body composition, and the second at the high energy (40 keV) to identify the network modifiers, colouring agents found inside the glaze. The beam size at the surface is 10.7 mm x 9.4 mm, and a camera is used for controlling the measured area. Due to the variation of the minerals found in the body and the glaze thickness, the measurements were carried out on at least three different areas of the paste and coloured areas of the glaze, with 30 s of radiation time (one day campaign of measurements in the excavation laboratory and excavation site by G. Simsek). The results, which are obtained as the mean values of all the individual point analyses were done on the body and each colour of the decor including the transparent glaze layer, are reported concerning weight percent (see Table S2). They were calculated via the method already installed in the instrument. For the semi-quantitative evaluation purposes, the K_α lines of major elements (Mg, Al, Si, K, Ca), transition metal elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) and trace elements (Rb, Sr, Zr, Ba, Bi), as well as the L spectral lines of lead and tin, were taken into consideration. The calibration of the instrument was controlled by using the mineral standards, which allow measuring ceramic materials with a high detection capability. For some easier comparison with the literature, some data were also transformed in wt % oxide. A pXRF system cannot measure sodium (Na) and lighter elements because of the air absorption, contrary to WD-XRF (wavelength dispersive – X-ray fluorescence) laboratory instruments, which can measure all the elements of the periodic table, up to boron [36]. A vacuum pump is required during the measurement of light elements, but it is not adapted for each pXRF instrument and for mostly on-site recording conditions, e.g., in the study of large tile walls. However, the amount remaining after the subtraction of the sum of the other oxides from 100 refers to an approximate content of Na_2O. This calculation is mainly applicable for the ancient ceramics because the major and minor constituents of the body and glaze composition are consistent, and the tiles are almost free of corrosion. In the case of the analysis of the corrosion products occurring on the metallic artifacts, the lighter elements could not be estimated due to the varied corrosion products.

The measurements of the body were iterated less than the glaze layer due to the consistency of the homogeneous paste composition. The glaze had to be measured several times, in different spots because of the heterogeneous structure of the ancient ceramic glazes originating from the complexity of the decor, which imposes very variable concentration of colouring agents, the firing conditions and constraints due to the thinness of the coating. Further, undissolved and/or dissolved minerals/pigments in the glaze cause discrepancies of the analyses. The distribution of both varied and unvaried measurements of the transparent glaze layer as well as the coloured glazes can be explicitly seen in Fig. S3 with the example of Pb vs. Si plot. The lines in the figures of scatter plots are drawn as a guide for viewing. Elements issued from a single raw material in variable proportion in the glaze, for instance, the colour precursor, network modifiers and fluxing agents of the glaze, will be located on a linear curve starting from the origin [25,31]. If the element remains undissolved in the glaze of which the thickness varies, the contribution of the substrate will affect the measurement of the glaze composition. Therefore, a statistical approach comes into prominence for the glaze analyses. When an element dissolves in the vitreous matrix of the glaze, it can be considered that whatever the measurement, it will remain constant and the points will be aligned horizontally or vertically depending on the choice of axes.

A statistical program, titled Minitab 17, was used for drawing graphs of PCA (principal component analysis) and dendrogram which shows the similarity and differences in the body compositions of the tiles, allowing an easy interpretation for archaeologists and researchers not expert in ceramic technology.

3. Results

3.1. Body

Before the measurement with the pXRF, a visual examination was performed to identify the colour changes in the paste. When we compared the colours visually, three types of paste were determined, in red, light beige and white colours. In the same atmospheric conditions during the firing process, a high addition of limestone in the body clarifies the colour of the paste from red to yellow, and when it is added in low quantity, the colour of the body turns to red with the same iron content. Alumina (Al_2O_3) versus quartz (SiO_2) scattering plot (Fig. 2 upper) confirms the use of different raw materials in the body composition of the tiles, varying from the production period. However, high alumina content indicates the addition of a high amount of alumina-rich clay and high silica content showing a high level of quartz grains.

In addition to the visual examination, the elemental analysis concluded that three groups of body composition were defined with the pXRF measurements (Table 1), as follows:

i *Group #1*: 14th-15th-centuries productions contain a low amount of quartz (around 50% SiO_2) and high alumina (12–16 wt% Al_2O_3) which means the use of a clay-rich paste. Studies on the early period productions of Iznik confirms the results of Group #1 [8,16–18] and linked this production to Timurids production.

ii *Group #2*: 16th-17th-centuries productions contain a high amount of quartz (65–85 % SiO_2) and low alumina (3–6 wt% Al_2O_3): a typical fritware/stonepaste recipe well established for "Iznik" tiles [8,9,11,18,37–39].

iii *Group #3*: A third group including the tiles B8-1 (assigned 16th-century), B7-8 (second half of 16th-century), and B7-7 (17th century) have low content of Al_2O_3 (3.6–6.3 wt%), a medium level of SiO_2 (39–62 wt%) and an additional amount of calcium (27.5 wt% in the body of B8-1, 37.2 wt% in B7-7, and lower amount in B7-8, 11 wt% CaO) which represents the presence of a calcareous paste rather than a siliceous – clayey body (see Fig. 2).

Comparison between present pXRF measurements (solid labels) and measurements made at the laboratory with fixed advanced instruments (specific labels) in Figs. 2 & 3 will help to assess the reliability of pXRF versus the analyses at the laboratory facility. The scatter plots of K/Si versus Ca/Si (Fig. 2 middle) and Ca versus Fe (Fig. S5 bottom). The sum of Na_2O (sodium oxide) and K_2O (potassium oxide) refers to the content of the alkalis in the ceramic bodies and glazes. The body analyses confirmed the three groups which contain a significant level of alkalis (11 wt%, Group #1), lead-alkali (9 wt%, Group #3) and poor in alkalis (7.5 wt%, Group #2).

A statistical approach, which allows the archaeologists to form a better interpretation of the results, is adopted by a graph of dendrogram (See Fig. 2 bottom) which shows the similarities of the shards regarding their body composition. The major (Mg, Al, Si, Ca, K, Fe, Pb) and minor (P, S, Ti, Rb, Sr, Zr, Ba, Bi) elements were selected for drawing the diagram. This graph clearly demonstrates that two tiles (B8-1 and B7-7) of Group #3 are very different from the shards of Group #1 and #2. B7-8 is also in the same group but closer to Group #2 in terms of the body

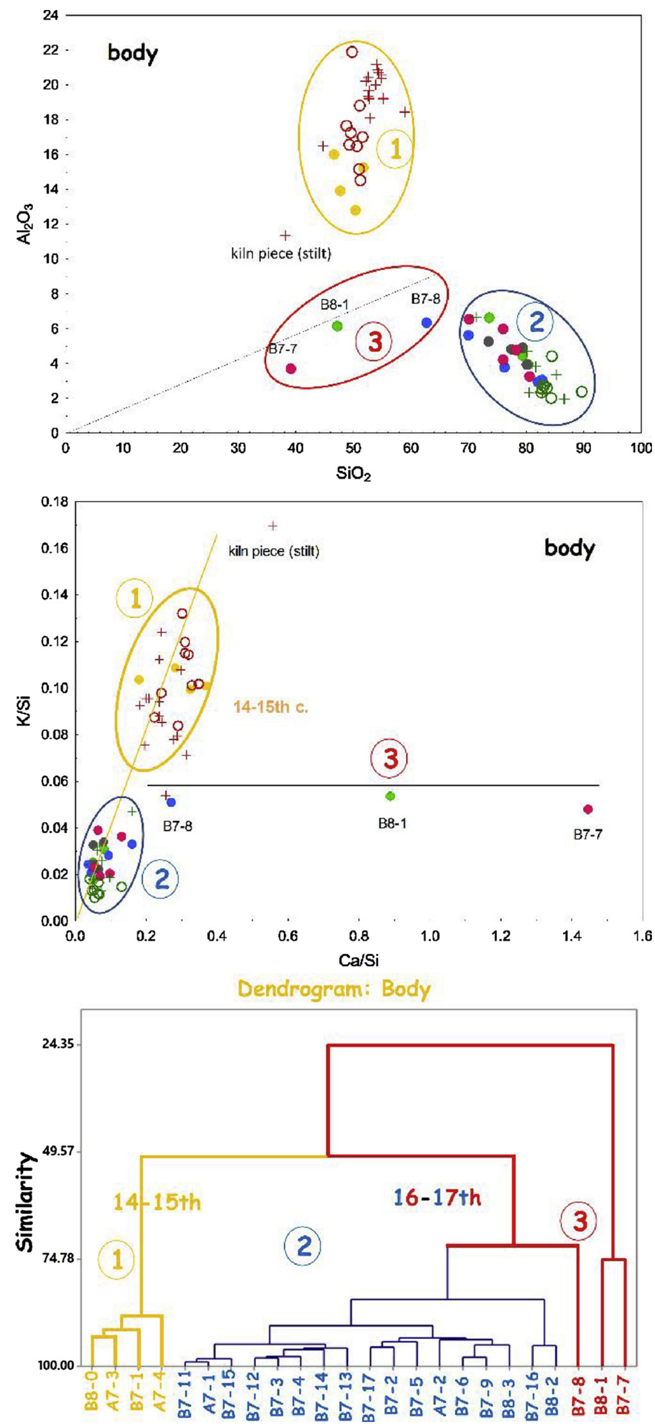


Fig. 2. Scatter plots of the weight % ratios of Al_2O_3 versus SiO_2 (upper) and K/Si versus Ca/Si (middle) in the body showing the tiles of five periods of production: 14-15th-c. (orange circle), 16th-c. (green circle), second half of 16th-c. (blue circle), 16-17th-c. (grey circle), 17th-c. (red circle) and one formation material of the kiln dated to unknown century (brown circle). Previous studies carried out with SEM-EDS were plotted in red open circles [28] & cross [2] (for redware) and green open circles [28] & cross [2] (for stonepaste). Lines and circles are drawn as a guide for viewing. A dendrogram of the similarity on the body compositions (bottom) is plotted for better interpretation of the results by archaeologists. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

constituents. This dendrogram, which shows the Euclidean distances of the studied tiles, confirms the findings carried out by the scientific analyses. The scatter plot of Ca versus Fe (Fig. S4 upper) shows that the

Table 1
Conclusion of the findings with pXRF measurements.

Body Group	Frit	Glaze	Sn content	Characteristic Minor elements	Cobalt origin	
1 Alumina-rich	K-rich Pb-poor	Alkali- & lead-rich	High & no tin	Bi low	No blue area	
2 Silica rich	K-poor	medium	low	Bi high	Co-Ni-Fe-As	Mn/Co < 0.1
					No As	Mn/Co > 1, Mn/Co < 1
3 With chalk	Pb-rich	Pb: variable	low	Bi high	No As	Mn/Co > 1

earlier productions contain much more iron but less calcium, which also evidences the red colour of the body. The visual examination differentiated the pastes in off-white (or light beige) colour in which the analyses found a high content of calcium with very low amount of iron representing Group #3. In Group #2, there are two sub-groups which differ in terms of the preparation of the raw materials. One may correspond to the purification of the clay of Group #1 by removing the iron content by washing or selection.

A similar classification to the Euclidean distances graph can be obtained by using the PCA method (see Fig. S4 bottom). The scatter plots of the body and glaze constituents are more efficient for the interpretation of the results but require an intense knowledge of the ceramic technology. However, the use of PCA and similar statistical methods will be more comprehensible for the archaeologists and researchers less expert in the ceramic production technology.

3.2. Glaze

3.2.1. Tin/lead ratio

Fig. 3 (upper) represents the distribution of tin versus lead normalized by silicon content measured in the transparent glaze or the glaze having the white decor beneath. Tin content varies between 0.06 and 6.26 wt% (0.072–7.95 wt% SnO_2) and lead is found between 21 and 42 wt% (23–46 wt% PbO). The values of the ratio of tin versus lead measured on the glazed shards of this study are given in Table S3, with the comparison of the literature [11,14,25,27]. Lines coming from the origin at zero have been drawn intentionally as a visual guide for the easier interpretation of the results. The scatter plot of Sn/Si versus Pb/Si shows three different groups which justify the decrease in the use of tin oxide by centuries. The lines show that the tiles were made with two Pb-Sn sources but varying in the quantity added. Tin mining places are rare, making the cost of tin high, and it seems reasonable that potters limited the Sn content. Sn can be also associated to Pb, in particular if bronze waste is used [40]. These three groups defined by tin to lead ratio correlate with the groups determined by the analyses of the body composition. We note only two exceptions: A7-4 from Group #1 and B7-3 from Group #2 are not included in the scatter plots of the glaze components because they were not glazed.

Group #1 (first productions, 14th-15th centuries) shows two glaze technologies, one with high amount of tin and lead (B7-1: 7.95 wt% SnO, 32.5 wt% PbO; A7-3: 4.93 wt% SnO, 33 wt% PbO) already observed [25] and the other without tin (B8-0: 0.15 wt% SnO_2) but with the highest amount of lead (46 wt% PbO). More statistical study requires to exclude that this sample is not representative (waste). All the shards of Group #2 have a similar amount of lead and tin, except B7-2. The lead content in the glaze of B7-2 is in the same range of Group #2, but the tin amount is higher than the other tiles of the group. With regard to tin content, B7-2 is closer to Group #1. Group #3 is divided into two subgroups, B8-1 and B7-8 having a considerable amount of tin, and B7-7 with low tin probably coming as the impurity of the lead source.

The production of the second half of 16th-century is generally the most controlled technology of Iznik provenance showing a slight variation of the glaze composition (Fig. 3 upper) [19]. Only the tiles B7-10 and B7-15, in the characteristic manner of polychromic Iznik productions, contain a very low amount of tin (0.05 wt% and 0.52 wt%

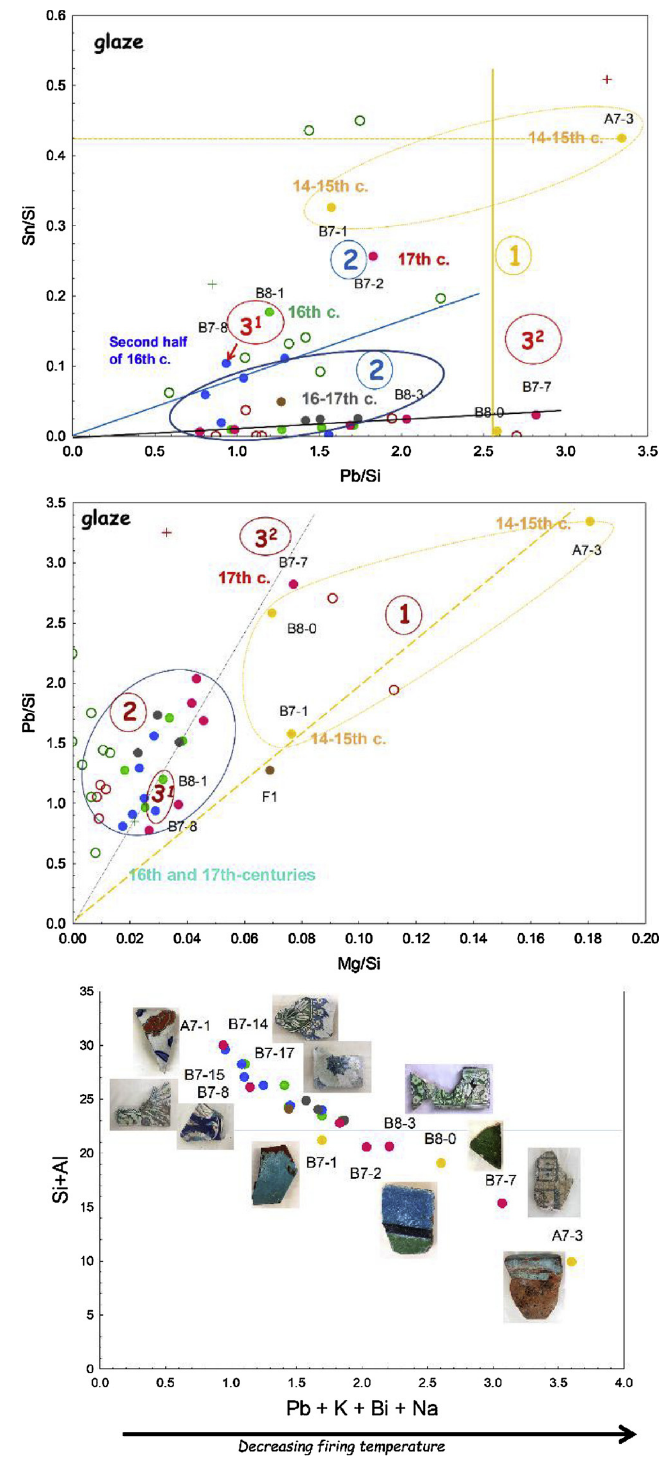


Fig. 3. Scatter plots of the weight % ratios of Sn/Si versus Pb/Si (upper), Pb/Si versus Mg/Si (middle), and network formers (Si + Al) versus fluxing agents (Pb + K + Bi + Na) in the transparent glaze (bottom), see previous figures for symbols. Lines are drawn as a guide for viewing.

respectively).

The 16th and 17th-centuries productions detected as clustered in the lower part of the Sn/Si versus Pb/Si scatter plots (Fig. 3 upper) representing the lowest content and small variation of tin (0.2-0.5 wt% SnO_2) with more extensive distribution of lead (22–45 wt% PbO).

Pb/Si versus Mg/Si scatter plots (Fig. 3 middle) confirm the distribution of the three groups, typically. Group #1 and the subgroup 3^2 have a higher amount of Mg and Pb while Group #2 and subgroup 3^1 are clustered together in the low Mg/Si region. The straight line drawn from the origin indicates that the frit brings both lead and magnesium. The brown layer (F1) is a formation of the glaze on the clays of the kiln walls which is aligned on the line coming from the origin and closer to B7-1.

The amount of sodium is calculated for the glaze composition, as we did on the body, and plotted in the scatterplot of alkali content versus lead oxide (Fig. S5 bottom). The dispersion of the results is broader than the body content because the thickness of the glaze varies. Moreover, the penetration depth of X-rays changes resulting the interaction of the body composition in the glaze analysis. This graph evidence mainly the presence of two types of glazes, alkali-rich lead (B8-0, A7-3 of Group #1 and B7-7 of Group #3) and lead-rich alkali (rest of the Groups 1, 2, 3) in the studied shards with changing amount of tin in the glaze (Fig. 3 upper).

The detection of bismuth with the pXRF may give valuable information about their use in specific tile production and the source of lead which could allow the identification of the provenance of the raw materials. Bismuth has already detected in the transparent glaze of some Ottoman tiles [18,25]. Fig. 4 upper shows that bismuth is an impurity of lead. However, bismuth can also be an impurity of a cobalt source. Therefore, the amount of bismuth should be compared both in white and blue areas. The analysis showed that bismuth is extracted from the glaze not from the blue colouring agent in the tiles A7-1, A7-2, B7-2, B7-7, B7-9, B7-10, B7-11, B7-16, and B8-3. However, the other tiles (B7-4, B7-5, B7-6, B7-8, B7-12, B7-14, B7-15, B7-17, and B8-2) having the blue areas contain bismuth as an impurity of the cobalt source. The scatter plots of K/Si vs. Ca/Si (Fig. 4 bottom) show mainly two different types of fluxes used in the glaze, some containing only potassium, and the others having potassium and calcium, according to the literature [41].

In the scatter plots of Al versus Si (Fig. S5 upper), the tiles of 14th-15th-centuries are aligned together with less amount of silicon. For the tiles of the Group #1, aluminium is an impurity of sand. The tiles of groups #2 and #3 clustered as the second group of the plot. The tiles of the second half of the 16th-century contain a low amount of aluminium and high amount of silicon, typical for the classical period of Iznik production.

3.2.2. On-site kiln wall measurement

An on-site measurement was carried out to identify the glassy green material formed on the walls of the fourth kiln (see Fig. S2). The analysis showed that this glassy surface surprisingly contains almost no lead (0.047 wt% Pb) but a high amount of sulphur (4.313%wt). Throwing *alquifoux* (PbS) inside the kiln at the end of the firing process is a classical technique which was used in Morocco for the traditional pottery production, in these days [42,43]. This knowledge may explain the presence of sulphur. As lead and sulphur vaporize easily, the former does not leave any residue on the wall inside the kiln, the condensation of lead being expected further (chimney). The other elements found on the surface are Mg (3.20 wt%), Al (4.44 wt%), Si (18.68 wt%), P (0.317 wt%), K (3.22 wt%), Ca (13.42 wt%), Ti (0.79 wt%), Cr (0.05 wt %), Mn (0.15 wt%), and Fe (6.83 wt%).

3.3. Colouring agents

3.3.1. Blue colour

Three types of cobalt were identified in the blue decors of the tiles studied (see Fig. 5).

i) No arsenic containing tiles: B7-11, B7-12, B7-16 (16th-c.); A7-1, A7-2, B7-8, B7-10 (second half of 16th-c.); B7-4, B7-5, B7-6 (16-17th-c.); B7-2, B7-7, B7-9, and B8-3 (17th-c.)
ii) Constant arsenic content: B7-3 (16-17th-c.) (and B8-2? (17th-c.))
iii) Constant cobalt content: B7-15 (second half of 16th-c.), B7-14 (17th-c.) (and B8-2?) and B7-17 (16th-c.)

Bismuth was detected in the blue decors of all the shards except B7-3, which was not glazed but painted (see Fig. 5 upper). This suggests that bismuth may be an impurity of the lead source, and not a trace element of cobalt found in the blue decor. When comparing the bismuth amount in the transparent glaze to the blue decor, it is detected that two different types of cobalt exist in the blue decors. One group contains bismuth and the other does not. It is found that bismuth is present only in the glaze of A7-1, A7-2, B7-2, B7-7, B7-9, B7-10, B7-11, B7-16, and B8-3 (16th-17th-c.). The blue decors which contain bismuth as an impurity of cobalt belong to the tiles B7-3, B7-4, B7-5, B7-6, B7-8, B7-12, B7-14, B7-15, B7-17, and B8-2 (16th-17th-c.). The scatter plots Mn/Si versus Co/Si and Co/Si versus Ni/Si (Fig. S6) shows the use of different cobalt sources. The arsenic-rich decors are also rich in nickel (B7-3, B7-17). Moreover, the tiles B8-3 and B7-2 are rich in manganese which contain no arsenic.

3.3.2. Red colour

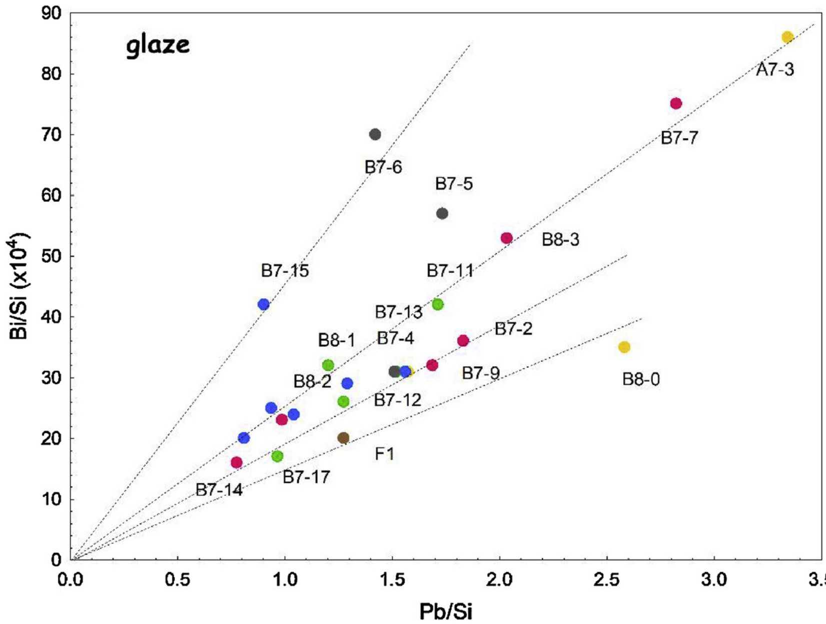
Fig. S7 upper left shows the content of iron and copper in the red decor. The two tiles of the 17th-century (B7-14 and B8-3) contain high amount of Fe and Cu, and the prototypes of B7-12 and B7-13 lower Fe & Cu in the red areas. For the other tiles, which correspond to the productions of 16th and second half of the 16th-centuries, iron may be an impurity rather than a deliberate addition. Up to know, only a mixture of quartz and hematite (Armenian bole [19,24]) or a silicate mineral called aegirine ($NaFe^{3+}(Si_2O_6)$) [11,26] was recognized in the red decors of Iznik productions, but for the first time, this study showed that the artist might potentially use the mineral of bornite (Cu_5FeS_4), which was found vastly in Anatolia during 16th-17th centuries [44,45]. Only for the tiles B8-3, A7-1, and B7-10, there exist a diffusion of copper towards the red area from the adjacent green/turquoise colour which was observed from the spot images of the pXRF instrument. For the tiles B7-14 and B8-3, the amount of iron is very high regarding the other tiles (averagely 1.8 wt%). The copper content varies between 0.1 – 0.3 wt % with about 0.4- 0.6 iron for the other tiles.

3.3.3. Turquoise colour

Similar scatter plots (Fe/Si versus Cu/Si) are drawn for the turquoise colour (see Fig. S7 upper right). Consequently, a mixture of iron and copper detects for the tiles of 14th-15th centuries (B7-1 and A7-3). However, the main turquoise colourant for the other tiles is copper and iron is found as an impurity.

3.3.4. Green colour

The scatter plots of Cu/Si versus Fe/Si (Fig. S7 bottom right) were drawn to identify the composition of the green coloured areas. The visual examinations on-site clued in on the presence of different green pigments, changing the hue and saturation from bright and light to dull and dark colours. pXRF measurements on the green areas showed that two types of green pigments were used: chrome and copper containing. The green decor of the tile B7-16 and B7-17 contain chrome-based pigment while the other tiles have different ratios of copper depending on their light and dark colours. The tiles B7-14 and B7-16 do not contain any iron with copper, but the other tiles do. The measurements showed that the green colour of the monochrome glaze shard, B8-0, was obtained by the addition of copper ions in the lead-rich glaze. Lastly, B7-2 and B8-1 contain both chrome and copper in the green areas.



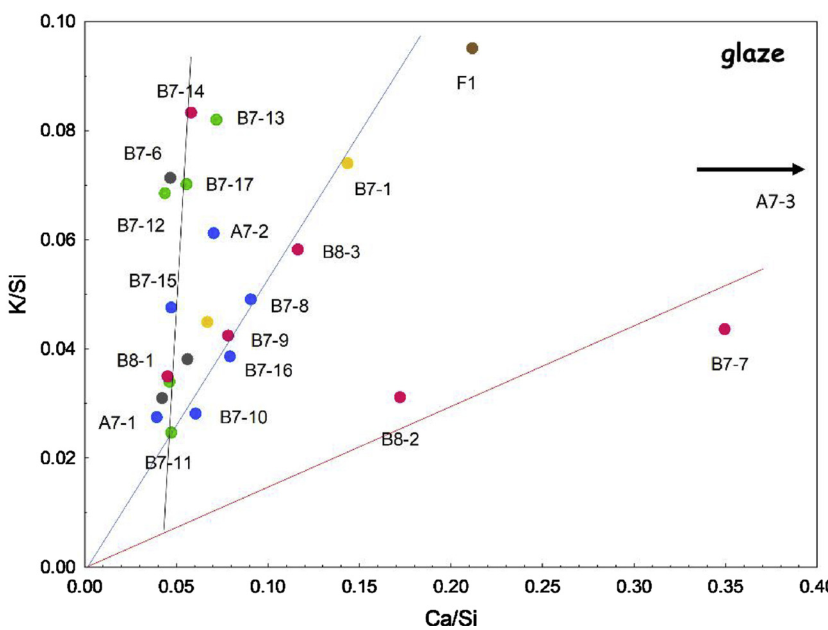


Fig. 4. Scatter plots of the weight % ratios of Bi/Si versus Pb/Si (upper) and K/Si versus Ca/Si (bottom) in the transparent glaze, see previous figures for symbols. Lines are drawn as a guide for viewing.

3.3.5. Black lines

The black lines are measured for the tiles A7-1, A7-2, B7-9, B7-14, B7-15, B7-16, and B8-3. Chrome containing pigment is found only in the line decors of B7-14 (0.35 wt% Cr), B7-15 (0.6 wt%), and B8-3 (0.16 wt%). The same tiles contain a higher amount of iron. It is clearly seen that an iron-chromate spinel was used in the black lines of these tiles. The other shards, A7-1, A7-2 B7-9, and B7-16 contain only iron in the black lines.

4. Discussion

4.1. Validity of non-destructive elemental analysis with portable instrument

On-site measurements with portable instruments become crucial in terms of the reproducibility and reliability of the results obtained. The accuracy of the data obtained with the pXRF can be provided by using the proper calibration standard (glass standards Corning Brill B, C, D, NIST SRM 611; geological standards red mud, diorite DR-N [46,47]) which allows doing a semi-quantitative analysis for determining the composition of the body, glaze, and pigments used in the decor. In this study, pXRF results of the tiles were compared to the past analyses of the Iznik kiln excavation materials carried out with SEM-EDS in the laboratory conditions by plotting all the data in the same scatter plots (see Fig. 2 for the body, Fig. 3 for the glaze) [2,28,29]. As already known [25], pXRF instrument cannot measure sodium content in the ceramics, but it can be calculated as explained above in the experimental part. Even the comparison of our calculations shows a shift regarding the body analyses carried out with SEM-EDS (Fig. S4). Due to different calibrations of the instruments, it is clearly seen that the earlier productions of Iznik kilns, which were mainly produced of clay-rich raw materials, contain higher amount of alkali ($Na_2O + K_2O$) and the fritware type (or stonepaste) have less alkali in the body. With this method, the three groups of paste were also well-evidenced. The variation of the results is affected from the penetration depth, which is

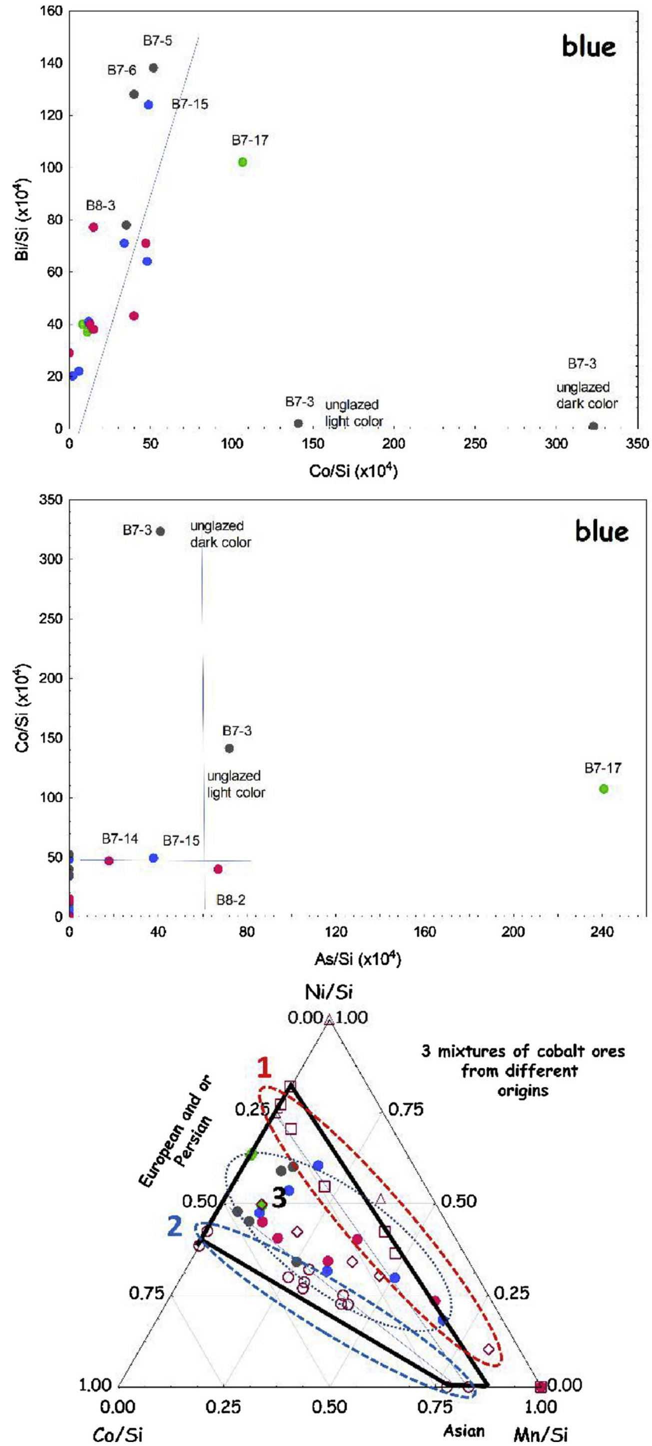


Fig. 5. Scatter plots of the weight % ratios of Co/Si versus As/Si (upper), Bi/Si versus Co/Si (middle) measured on blue areas, and ternary diagram (bottom) of Co/Si, Mn/Si, and Ni/Si showing the distribution of blue pigments of this study (solid circles) and reference data from the tiles of Edirne (open labels) [25]; see previous figures for symbols. Lines are drawn as a guide for viewing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

higher in pXRF than in the EDS system. The heterogeneity of the glaze, which is derived from the corrosion, the solubility of the constituents, and the interaction volume with the body, leads to a larger distribution (Fig. S5 bottom) than the elements in the body, in which the structure is more homogeneous perpendicularly to the surface.

4.2. Monochrome to polychrome tiles

The tile production in the Anatolian territories, which was trademarked as Ottoman and/or "Iznik" was divided into four phases between 12th- and 17th-centuries [41]. The phases include 1) the period of Anatolian Seljuks during 12th-13th-centuries with the importation of Persian techniques, where the most representative tile ornamentation covered the walls of Gök Medrese in Sivas, 2) occasional production of the tiles in the early 14th-century by potters who were using the technology of lead-glazed earthenware with red clay in the body, 3) period of Masters of Tabriz in the early 15th-century, and 4) after a gap in tile production in the late 15th-century of some thirty years, re-beginning of the tile production in the 16th-century in Iznik kilns [41,48]. Unfortunately, the workshops where the Seljukian,Persian, and Timurid craftsmen worked were not documented in the ancient manuscripts, [48]. The only evidence of the group of Masters of Tabriz is their signature on the tilework of the Yeşil (Green) mosque and tomb of Mehmed I (1419–1424) in Bursa still without any knowledge of the production place of these tile revetments. Primarily, the study of the 14th-15th centuries tiles is crucial in the investigation of the transition/link between Anatolian Seljuk and Ottoman ceramic production technologies. Therefore, some earlier Iznik's productions were chosen for examination, dating back between 14th-15th centuries to identify the technology used in the body and glaze. We noticed that the technology of the monochrome shards of this study, especially B7-1, which was glazed in turquoise colour, is similar to the turquoise, hexagonal and triangle glazed tiles of Şah Melek Paşa (Edirne) and Muradiye Mosques (Edirne) (see Fig. 6 upper). In addition to the earlier productions, the tiles of the classical period of Iznik (16th- and the second half of the 16th-century), as well as the later productions, were analysed during this preliminary study of the one-day campaign. Because of time constraints, the number of tiles analysed with pXRF was confined to the different representative technologies of Iznik tiles. The selection criteria were based on the presence of glaze, polychromic and monochromic decors and the different patterns drawn. Three glazed tiles painted with the main colour lines, where the artist might try to find the best saturation and hue of the main, red, green, and blue colours, were included in this preliminary study to compare the colouring pigments with the coloured areas of the other tiles' decors.

4.3. Glaze

Previous studies on Iznik tiles showed that a slip layer exists between the glaze and body layers and is used as a lining for a finer decoration [19,26,27]. In this study, the tile B7-3 is an example of a painted-on top of the slip layer. The biscuit form of a ceramic represents the first firing step before the glazing of the tile [11]. Under-glaze decorated Iznik tiles contain a slip layer and are double fired; firstly, to obtain the slipped body and secondly for firing the glaze [11]. However, the monochrome Group #1 includes coloured glazes without any slip layer, which can be seen from Fig. 1. In this group, the tile A7-4 is fired without the glaze. If the tile is single fired, the interaction of the body and glaze layers gains importance in order to prevent any firing defects. The artist may have been firstly tryingto find the best recipe of the paste, before glazing, by producing biscuits. The shards without having a slip layer are always single fired.

Fig. 3 bottom shows the ratio of the fluxes (Pb, K, Na, Bi) to the network formers (Si + Al), which is related to the firing temperature. The glazes of the monochrome tiles of the Group #1, which were attributed to the productions of 14th-15th centuries, contain high amounts of fluxes, leading to a firing step at lower temperatures, equal or less than 700 °C [49,50]. Blue circle labels in the Fig. 3 bottom, which represent the productions of the classical Iznik period, from the second half of the 16th-century, contain high amount of network formers, requiring a higher firing temperature, which is around 800 °C, and even more than 900 °C. The limited variation of the composition

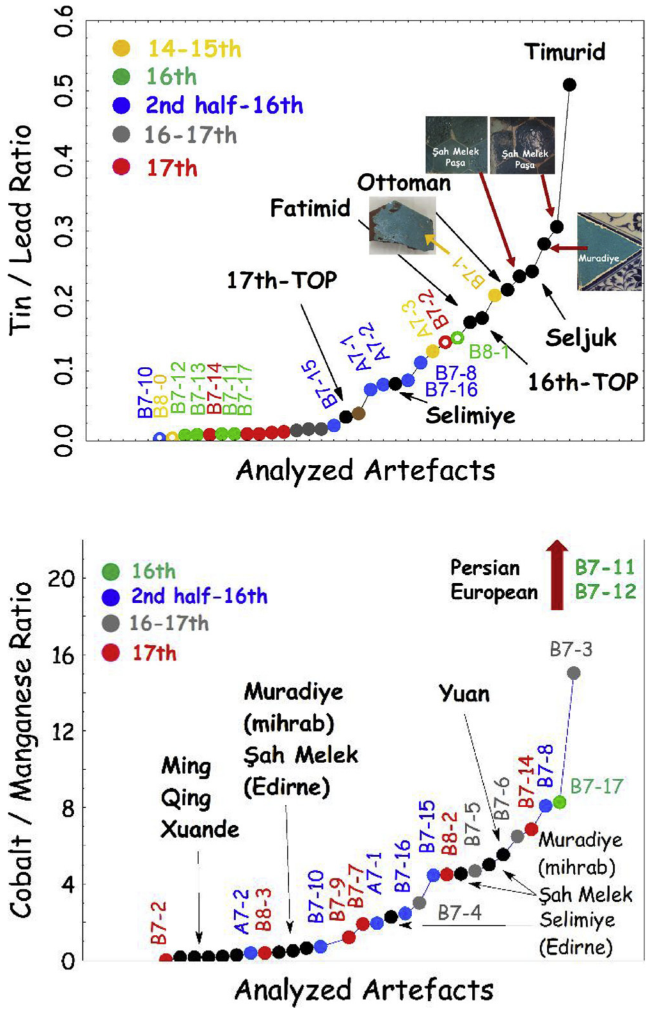


Fig. 6. *Upper* Evolution of the Sn/Pb (reference data obtained from 11,14,25,27) and *bottom* Co/Mn ratio [53–70].

demonstrate that the classical Iznik productions are strictly controlled. The firing temperature could be accurately determined by measuring the thermal expansion with dilatometry or DTA/DSC.

4.4. Body

Evliya Çelebi, in his book (*Seyahatname*), states that around three hundred ceramicists worked in the workshops of Iznik [33]. Recent excavations also showed that almost thirty tile kilns were explored in the last years [51]. The technology of the Seljukian tiles having a black decor under the turquoise glaze has been encountered in the excavations of Iznik. The technique was in use from the 14th-century for a long time in the production of daily use ceramics. The body colour of the tiles and ceramics is usually ash yellow in the Seljuk period, reddish in Beylic and early Ottoman period, and dirty white during the classical period of Ottoman era [32]. When compared the body composition of the tiles from 14th-15th-centuries (B8-0, B7-1, A7-4, A7-3) with the literature [14,52], no similarity was detected with the Persian technology during both Seljuk (1050–1200 AD) and Timurid (1400–1440 AD) periods. The Damascus production in Syria during the Mamluk period (1250–1350 AD) is closer regarding the calcium content, but the alkali amount is still less than the tiles of the Group #1 [14]. However, Group #1 tiles have a similarity with the tiles 82, 83 from Yeşilce Mosque (Edirne) and Syrian productions regarding the body which is composed of higher content of calcium, iron, and aluminium which differs in technology from the other tiles studied in this research [25,52]. Typical 16th-century productions of Iznik are consistent with the documented tiles of Selimiye Mosque, which represents the most successful period of Iznik workshops [25]. The minerals found in the bodies of the tiles excavated at Iznik tile kilns were already identified by national researchers with petrographic investigation and XRD analyses [2,28]. The composition of the body is formed of the matrix constituents and the minerals are added. The matrix is composed of a mixture of local clay, frit and some iron oxides. Quartz and albite and/or anorthite are the major minerals followed by mica minerals (biotite). The redwares (representing the shards of the Group #1) differentiate from the stone-paste (Group #2) with the use of raw rocks (e.g. granite) and grogs [28]. The epidote mineral, which is found mainly in cipolin (marble species formed in contact with intrusive rocks), is detected in a few tiles. This explains the high level of calcium for the Group #3.

4.5. Tin oxide

The use of tin oxide in the glaze decreases through centuries, which may have been caused by the high cost of tin and by the perfect mastery of the white quartz slip. Fig. 6 upper features the distribution of Sn/Pb ratio representing the different groups and is compared with the literature including past measurements carried out on Ottoman tiles, “Iznik” tiles at Edirne, Fatimid, Seljuk, and Timurid tiles [11,14,25,27]. The tin content of 16th-17th- centuries productions are similar to the Ottoman reference tiles from 16th- and 17th-centuries because of the homogeneity of production at that period [19,20]. Earlier productions of Iznik, namely Group #1, tin-rich, are closer to the Seljukian tiles. B8-0 of the group 1 from 14th-15th centuries evidences an inconsistency of the tin content in the glaze, as well as B8-1 of 16th-century (Group #3) and B7-2 of 17th-century (Group #2). The tin content of B8-0 is lower than expected, and for B8-1 and B7-2, it is higher. The tiles of the classical period of Iznik (2nd half of the 16th-century) have a similar amount of tin, except the tile B7-10. The workshop where this tile was produced or the period may differ for B7-10. Since the studied samples were kiln waste, a wrong artefact is possible.

4.6. Colouring agents

The tiles B7-11, B7-12, and B7-13 may be a study collection of the potter(s), where he/she tried to define the hue of the main colours, green, blue and red. He might also have tried to define the best recipe of the paste suitable with the decor and glaze because the body composition varies in these three shards, mainly with respect to potassium, calcium, and lead content, which may reflect the use of lime-alkali (B7-13) and lead-rich frit (B7-11) in the paste. The analyses of the coloured areas, especially red and blue decors, showed that the composition is stable reflecting a controlled production process. Lack of differences in the blue and red area measurements may be due to the higher thickness of the glaze under, where the penetration depth of X-rays does not reach so much toward the coloured area. However, surprisingly, a copper-iron containing mineral, possibly bornite, is evidenced in the red areas of the shards B7-12 and B7-13. The artist might have discovered this mineral and tried to view the effect in the mixture of different colours. The last but not the least, another finding was discovered on the red pigments of the classical period of 16th-century. Iznik productions are well-known because of their famous red pigment in which hematite (Armenian bole, an intimate mixture of hematite and quartz) was added [19,26]. The analysis of the shards from the classical period of “Iznik” also shows the use of bornite (Cu_5FeS_4), which was widely found in Anatolian mineral deposits at that period [44,45]. Only, in the decor of B8-3, A7-1, and B7-10, the diffusion of copper may occur from the pollution of the adjacent colours across the red area. The investigation of the pigments found in the red areas with high-resolution instruments (e.g., micro-XRF, micro-XRD, SEM-EDS, Raman and TEM, on polished sections) can justify the type of the red pigment.

4.7. Cobalt origin

Mainly, there are three sources of cobalt applied with pigments in the blue decors of archaeological ceramics. 1) European cobalt: the mixture of Co-Ni-Fe-As, 2) Asian cobalt (Chinese and Vietnamese): the mixture of Mn-Co-Fe, no As, 3) Kashan (Persian) cobalt: Co with a high amount of As, Fe; no Ni, Cu, Zn [53–61]. Constantinescu mentioned that Porter, a researcher on Islamic art, stated the use of Erzgebirge (European source) cobalt ores and added that a change in the composition of the blue glazes was observed in 1520 by the presence of As and Bi by reduced amounts of Fe and Ni [15].

Two types of cobalt were determined with the measurements of the pigments present in the blue areas, depending basically on the arsenic content: Some tiles contained arsenic and the others did not. The detailed analysis showed that the blue decors of the tiles B7-3, B7-14, B7-15, B7-17, and B8-2 contain a mixture of Co-Ni-Fe-As, consistent with the use of European cobalt source. Ni is only rich in As-containing blue areas. Additionally, copper was also detected. These tiles belong to group 2 and are dated back to the 16th-17th centuries productions. No Persian cobalt source was used in the blue areas because the Kashan cobalt is expected to contain a high amount of As and Fe with no traces of Ni, Cu, and Zn. Thus, it may be assumed that the Persian influence did not affect the choice of the raw materials used in the tiles; only the technology was appropriated.

The blue decors with Fe, Cu and without As content are divided into two types: $Mn/Co < 1$ and $Mn/Co > 1$. The two tiles of the group 3 (B7-8 and B7-7) and the tiles from the group 2 (B7-4, B7-5, B7-6, B7-9, B7-16, and A7-1) are sorted in the group of $Mn/Co < 1$. When compared to the literature, the cobalt source could not be defined for this group ($Mn/Co < 1$ without As). Three tiles of the group 2 from 2nd half of 16th- and 17th-centuries, B7-10, B8-3, and A7-2 contain $Mn/Co > 1$ (1.38, 2.57, 2.6 respectively) which may be related to the Chinese cobalt source used in the late Ming dynasty at Jingdezhen, where no arsenic was detected and $Mn/Co > 3$ [62].

Fig. 6 bottom shows the evolution of cobalt versus manganese of the analysed artefacts and triple diagram of Co, Ni, Mn normalized by Si (Fig. 5 bottom) with the comparison of the reference data collected from the blue decors, where the pigments are originated from Chinese, Persian and/or European pigment sources [63–70]. The triple diagram shows three groups of blue decors. The main group of the tiles studied in this research clustered in Group #3 with the reference materials of Şah Melek Paşa and blue and white tiles of Muradiye Mosque at Edirne [25]. B7-4 and A7-1 plotted at the intersection of the Group 2 and 3 with the reference material of Selimiye Mosque (Edirne). These groups do not refer to the groups that were already defined by the measurement of the body. The numbers are specifically attributed to the scatter plots of the ternary diagram in Fig. 5 bottom. B7-16, B7-9, and B7-10 are at the intersection of Group #1 and #3 while B8-3 and A7-2 are plotted closely in Group #1 with the reference tiles of Üç Şerefeli Mosque [25].

5. Conclusion

The monochrome and polychrome Iznik tiles are the masterpieces of the Ottoman period which were produced from the 14th- to 17th-centuries by the orders of the Sultans for historical buildings. Therefore, most of the tiles were conserved in the wall revetments except the similar tiles excavated in the Iznik tile kilns. They represent mostly the samples of overproduction or waste materials of the workshops. By reason of the need of on-site, non-destructive measurements, a methodology had to be created by using a pXRF instrument at the same conditions with the analyses in the mosques, holy places, etc. compared to the measurements in the laboratory facilities. The capability of the portable instrument has been tested with the past analyses carried out on the similar materials excavated in the same kilns at Iznik with SEM-EDS and the efficiency has been proven by plotting the ratios of the elements in the same range. Although a technical knowledge on the ceramic production is required for the interpretation of the scatter plots, archaeologists and art historians are also able to interpret the results by using PCA/Euclidean distances graphs. The comparison of these two interpretation models showed that a reasoned selection of the parameters related to the ceramic raw materials appears to be more effective than blind statistical analyses (PCA/Euclidean distance).

In this study, three groups of body composition were evidenced: 1- rich in clay, poor in quartz and 2- poor in clay, rich in quartz as previously demonstrated and linked to Timurids heritage and characteristic of Iznik potter innovation, respectively; and 3- a new group, a mixture of quartz, clay, and chalk. Our study encountered, also, with different glaze technologies because of the changes imposed by the different body compositions. The thermal expansion is very dependent on the quartz content due to the alpha-beta transition during the firing process [71]. Three different glazing technologies are Sn-rich, Sn-medium and Sn-poor glazes. The amount of tin oxide in the glaze decreases over the centuries. Besides, two different types of fluxes were used in the glaze, some containing only potassium, and others having potassium and calcium.

The blue areas, which give more information about the provenance of the raw materials, were determined to be from three different cobalt ores, where European (Co-Ni-Fe-As), Chinese ($Mn/Co > 1$, no As) and an unknown source ($Mn/Co < 1$, no As) were identified. Another highlight of the study arises from the new evidence of the pigment found in the red decor. By this time, the use of a mixture of hematite and quartz (Armenian bole) was known for colouring the red areas. But in this study, we found that some faded red colours contained a mixture of copper and iron which referred to the use of bornite (Cu_5FeS_4) mineral which was rich in the Anatolian deposits during 16th-17th- centuries.

The last but not least finding of this study is the technological similarity of the monochrome shard, B7-1, with the hexagonal and/or triangle, turquoise tiles of Muradiye (Edirne) and Şah Melek Paşa (Edirne) Mosques [25] which reflects that Iznik tile kilns were pioneers since the beginning of the Ottoman period.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jeurceramsoc.2019.01.050.

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