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RESEARCH

First-time evaluation and characterization of "Šariššа" mudbrick ceramics and findings by SEM–EDX and XRF: chasing the traces of fire

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Abstract
Šarišša is one of the most important cities of Hittite Empire in the range of 16th–twelfth century BCE. The city's importance comes from being the Empire's summer palace as well as castle formation is seen around the city which gives the Turkish name "Kuşakli" means "Surrounded-Belted" in English. Šarišša is said to be destroyed by a fire/incendiary or battle and almost all mudbricks were given fire and their initial structures were deformed. The fired form of these ceramics could not be identified due to different degrees of fired ceramics and their identification may also favor the provenance analysis of the region's soil structure that is suitable for the production of mudbricks. For the analysis of mudbricks, X-ray fluorescence (XRF) analysis was evaluated first to understand the principal, compound former, and trace oxides to compare with geological soil formation and rock types. By examining XRF, the oxides were characterized for compound formation even for mineral composition. As evaluated, main oxides are SiO_2, CaO, Fe_2O_3, Al_2O_3, MgO, and K_2O; compound former was the volatile SO_3 that has the formation possibility of gypsum as Sivas's most provenance soil type within illite-muscovite type clays. Besides, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) analysis were briefly evaluated and the firing temperatures were estimated. From SEM images and EDX analysis, a very good match with XRF analysis was found by means of elemental distribution and especially Na amount was approached as glassifier by sintering of materials in the range of 800 and 1200 °C due to the glassification, vitrification, sulfate removal, and low viscosity bubble formation due to glass melting.

Keywords Archaeometry · XRF · SEM–EDX · Mudbricks · Fire/incendiary

Introduction

Discovery and beginning of the "Šarišša" research

Šarišša is a place already mentioned in other written sources such as Hattusa cuneiforms. The text "Kuşakli" contains a guide for the master of the ceremony here to perform the rituals during the annual religious holidays. Particular attention is drawn to how the Great King, who travels privately from the capital, should behave. The course of several festival days is described in detail. As part of the official state cult, these rituals must have been of great importance, since several copies of the "definition of the holiday" were made and also stored in the state archives of the capital of the Hattusa Empire (near Boğazkale, formerly Boğazköy) [1].

It is already certain that the image of the Hittite colonization in Anatolia will remain very rough, due to the rapid destruction of the archeological cultural landscape through modern superstructure, robbery excavations, the extraction of mineral resources, and the intensive agricultural use, especially due to the increasing powerful tractors with the construction of new dams. The discovery and exploration of similarly well-preserved Hittite city complexes such as Šarišša will continue to be exceptional in the future [1, 2].

The eastern part of Cappadocia's Central Anatolian landscape has long been a blank spot on the archeological map. Only a few explorers came to the area, and a few chance finds reached the museums. Hans Henning von der Osten

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made the first research trips from Alisar in Western Cappadocia (Yozgat Province) to Eastern Cappadocia from 1927 to 1931 on behalf of the Chicago Oriental Institute; the first systematic excavation in Central Anatolia was achieved. He identified the remains of a late Hittite Iron Age city near the Havuz village, 23 km southeast of Kuşakli. With his initiative, a gate lion which can be seen above the landscape was brought to Ankara, where it can be seen today in the museum [3–5].

Kuşakli first became to the focus of the research in the late 1970s, when Volkert Haas (Berlin Free University) discovered the ruins during a trip to Sivas province. He suspected that the city of Kussara, which was very important for early Hittite history, was here. However, the ruins had not yet been registered as a cultural heritage, so in 1982, the Manager of Sivas Museum gave permission to the villagers to start a "treasure excavation" on the lower city terrace, without being aware of the importance of the square. Luckily, the excavation site selection fell into one of the few areas of the old urban area that were probably not found, so the search was unsuccessful [4].

Location and climate of "Šariššа" city

Kuşakli is located approximately 50 km south/southwest of Sivas provincial center and therefore east of the ancient Cappadocia region (Persian: "land of beautiful horses"). From an administrative point of view, this place belongs to Başören village of Altinyayla district, which was called Tonosa in Roman period as briefly shown in Fig. 1 [2, 5].

Today, if one approaches the old town, can see the ring-like belt surrounding the crumbling fortification area even from far. It rises impressively on the top of the Acropolis in the middle, with the Hellenistic tumulus at its highest point. Fragments still clearly visible on the surface of the ruins indicate that this complex may be dated to the Late Roman period [6].

The Hittite city is around 1,600 m at the south end of the high valley, and the highest point of the Acropolis is 1,654 m and beyond, the mountain ranges, where Šariššа lies, are now called the Kulmaç Mountains. In the Hittite texts, there are many words of a Šariššа mountain that can mean all these Kulmaç mountain ranges exceeding 40 km. It is possible that the name of the Hittite mountain can only express Karatonus Mountain, which is the highest and most striking altitude of this mountain range, about 20 km southwest of the Hittite city. It is reported that the Great Hittite King Tuthalija IV (second half of the thirteenth century BC) came to hunt in the region. As in later centuries, during the Hittites, hunting was already an entertainment for members of the royal family [6–8].

The mountainous area near Šariššа was not only important as a good hunting spot. The mountain ridge of the Kulmaç Mountains is a geographic boundary important for the entire Middle East: here the basin flows between the Black Sea in the north and the Persian-Arabian Gulf or the Mediterranean Sea in the south (Fig. 1).

All the streams on the slopes overlooking Šariššа flow into Anatolia's longest river, Kizilirmak, which was called Halys in ancient times and Marassanta in the Hittites. It pours into the Black Sea near the legendary city Zalpa (İkiztepe?). On the other hand, all the streams rising beyond the ridge just 2.5 km south of Šariššа flow into the Euphrates and therefore eventually into the Persian-Arabian Gulf. It can be said that Šariššа is just above the Upper Mesopotamian border [8, 9].

The area cannot be fully described as the preferred area to encourage the development of an early city due to its altitude of about 1600 m above the sea level. The continental climate is correspondingly harsh: long, harsh winters with periods of frost of − 20 °C, even short-term − 40 °C alternate with short and hot summers, but only daytime temperatures reach 30 °C or reach more. The sunset quickly and delicately makes it cool, so only 2 months in the middle of summer stay away from night frosts. The mostly clear sky ensures that it is pleasantly warm in the sun even in winter, if not the icy, often strong north wind blowing [10, 11].

Thus altitude is only responsible for the annual average temperature reaching around 7 °C. However, the climate in Kuşakli is clearly continental, with significantly lower precipitation as well as the strong daily and seasonal temperature fluctuations mentioned above. The average precipitation value here is about 400 mm. The whole Central Anatolia-Cappadocia region has a semi-arid highland climate, with two-thirds of the precipitation falling as snow in winter and spring. In the summer, there are usually few months with no rain, so the landscape dries up and most of the vegetation fades. Sparse rains will then become more severe so too much soil is washed away on the slopes and streams and rivers can temporarily swell and cause damage [10–13].

Materials and methods

By an organized trip to Šariššа in Altinyayla district of Sivas with the Sivas Museum Manager, Ali Alkan, by the written and received official permission of Turkish Cultural and Tourism Ministry-Sivas City Cultural Directorate with a protocol number of E-19007571–150[150]-1032907–12.01.2021, adobe samples were taken from five different points as shown in Fig. 2. After the samples were taken from landscape and around the ruins, they were labeled and stored in sealed plastic bags, photo shot and coding studies were done and special care was taken as much as possible not to spoil them as illustrated in Fig. 2. The mudbrick specimens were grounded to a cube of 1 cm^3, washed

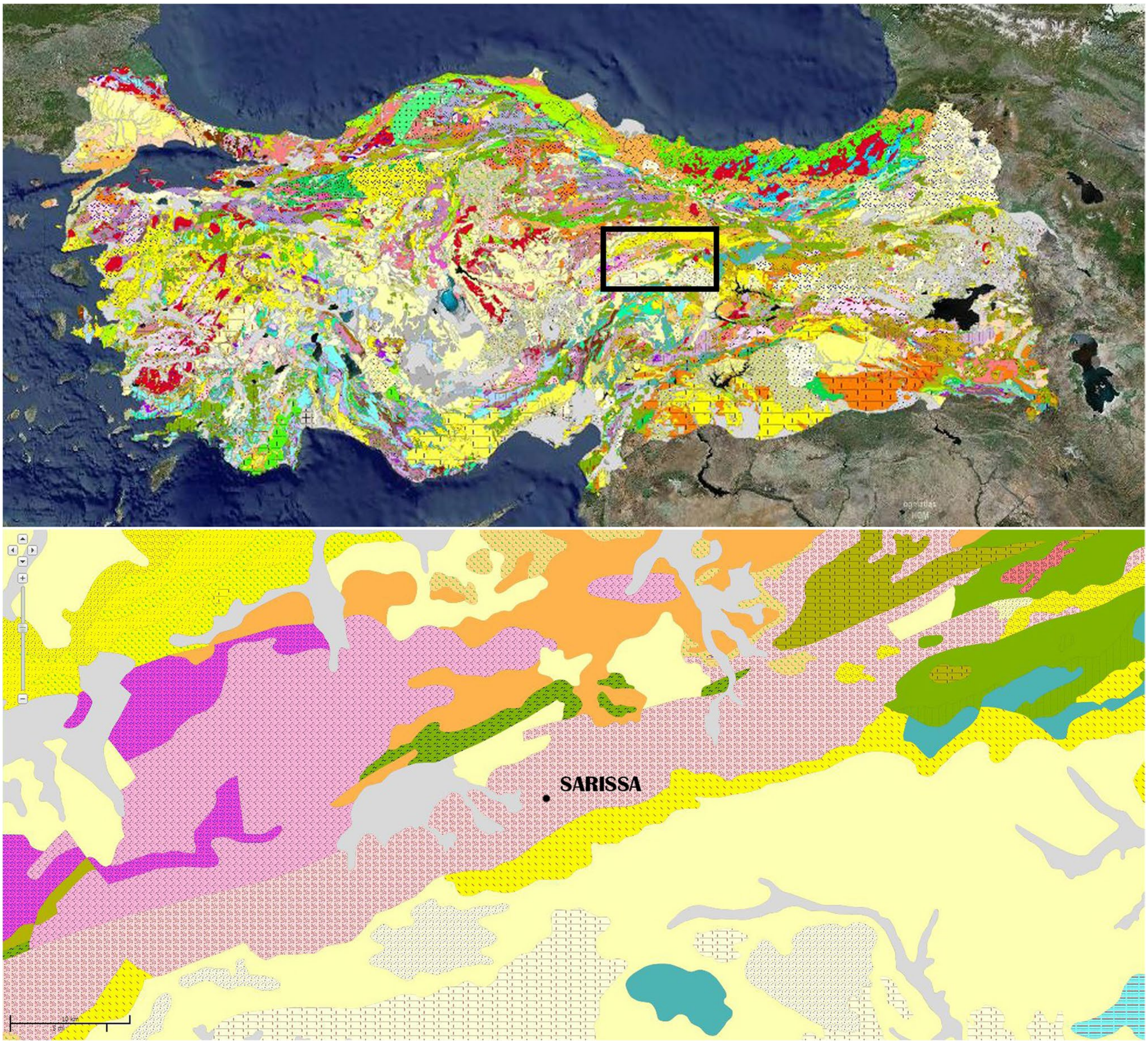


Fig. 1 The map of Turkey with geological formations and the place of Šarišša in magnified view of black rectangle as geological formation map [10]

and rinsed with ethyl alcohol to avoid excessive moistening of the samples, and dried quickly, thus removing any possible oil and dirt. The washed adobe samples were kept in the oven at 105 °C to dry for 1 day.

The map in Fig. 2 was taken by a drone and GPS techniques were used to locate the area. A surrounding wall is seen which gives the name Kuşakli to the city in Turkish, meant as "Belt-Surrounded." The ruins are seen and the closer photos were taken from drone for specifying the places of collected material in the middle part of figure. The latitude–longitude and altitude values were also given for better understanding the location on the Earth. Sample 1 was picked up from the entrance of the temple as red fired samples; samples 2–3 were taken right in front of the entrance of main gate, sample 2 was a mudbrick sample, and sample 3 was a white topped/black bottomed calcite/gypsum part; sample 4 was taken from the right entrance tower; sample 5 was taken from the landfill/road as greenish stones; and sample 6 was chosen from the temple hall as burnt and altered ceramic mudbrick with multicomponent appearance, and some parts of sample 6 were seen as vitrified and glassy bubbles, while some were hard and looks like slag. The reddish, black, green, and pink places were analyzed by XRF, XRD, and SEM–EDX for compositional and phase distribution.

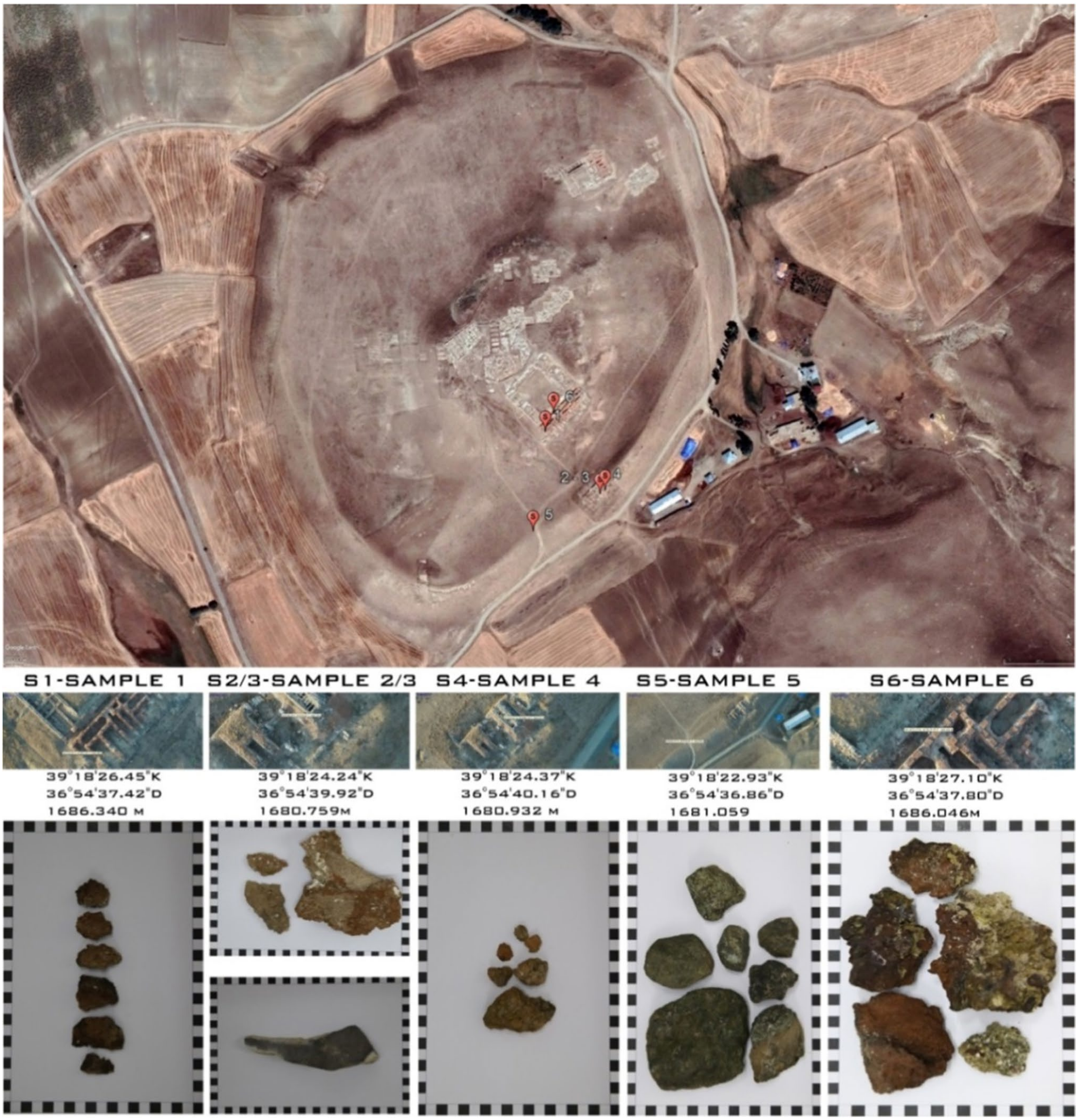


Fig. 2 The Šariššа map and surroundings from orthophoto by software and real-time dimensional macrophotos of samples (photos by Erdener Pehlivan, 01/05/2021)

The mudbrick specimens were taken from the site with a minimum deformation or as is, sized as properly as possible for analysis, and were attached to the aluminum stubs by sticking them onto double-sided carbon tape. A small piece of 5 × 5 × 10 mm of dimensions were grounded to pseudo-parallel for investigation of surface and structural features by a scanning electron microscope (SEM, Mira3 XMU, TESCAN®, Brno, Czechia) as well as EDX elemental mapping analysis (INCA x-act, Oxford Inst., UK) to evaluate and semi-quantify the oxides and elements on samples by coating with 5 nm gold in a sputter coater (Quorum Q150RS, Birmingham, UK).

The mudbricks were weighed about 5 g and grounded down to < 500 µm powder size by mortar and pestle to measure by XRF device (Niton Xl3t Gold + +, Thermo Fischer Scientific, USA) for elemental analysis of samples to identify the possible oxide compounds in them before and after a possible fire and/or incendiary.

Results and discussions

X-ray fluorescence (XRF)-elemental oxide analysis

Table 1 represents the XRF analysis of elements in samples, oxygen bonded and rated as wt%. The shown elements were exported from XRF post-process software and oxygen bonds were added by mol% and multiplied by their molar weight to obtain weights, then divided to total weight to obtain wt% of oxides. It is evident that six oxides were selected as principal oxides which were found to be more than 1 wt% of average in samples while sulfur indicates the compound forming ability as sulfates or sulfide bonds to evaluate the alteration possibility of especially + 2 oxides as Ca and Mg. Since SO_3 molecule produces stable oxides of CaO and MgO as $CaSO_4$ or $MgSO_4$, this may mean that the decarbonization of dolomite, calcite, or magnesite can occur in the presence of SO_3 or vice versa.

First of all, Sivas region should be said as the main karstic rock region with high amount of calcite and gypsum ore sources. Sivas map as in Fig. 1 can also be remembered that, in the south of Šariššа region, the Kulmaç Mountains with yellow color are calcite rich hills and pinky regions are sedimentary of high calcium containing clay minerals as seen in a valley as river bed. Šariššа is somehow in the middle and even lower than the surrounding mountains which make it windy and also called the "Home of Storm God Tešup" and has an erosive alteration, fragmentation by rains, and bad weather conditions as − 30 °C in winter and + 30 °C in summer time. This deformation conditions produce very fine particle size of even calcite and gypsum due to low crack energy and cleavages grinds the rock structures as well as produced and fired mudbricks.

S1 was a fired clay mudbrick sample that has two different regions of burnt, one was reddish sides and other was the blackish one. As of the XRF analysis result from S1-red, the sample consists of main oxides with high calcium containing clay-like structure. The absence of SO_3 can be said that these adobes were fired to high temperatures up to 1200 °C which may be the dissociation temperature of sulfates with red fired color. MgO and K_2O presence can also be interpreted to high coloring effect by high iron-oxide content. The trace element oxides do not exceed more than 2 wt% which also have a glassy effect to visualize them in reddish or pinky after firing. TiO_2, ZrO_2, ZnO, and SrO have white color and may contribute to brighter color than S1-black. The + 4 and + 2 element oxides as mentioned above are generally known as whitening oxides. As XRF analysis of S1-black, while Ca and Mg were decreasing, Si and K were increased with the

Table 1 XRF analysis of samples 1–6 for principal oxides, compound former oxide, and trace oxides by wt%

Samples	Principal oxides						Compound former	Trace oxides											
	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	K_2O	SO_3	ZrO_2	TiO_2	V_2O_5	Cr_2O_3	MnO	CoO	NiO	CuO	ZnO	SrO	Y_2O_3	BaO
S1-red	26.31	24.15	24.05	10.79	11.08	1.63	0.00	0.03	0.80	0.10	0.19	0.32	0.03	0.08	0.03	0.12	0.22	0.05	0.03
S1-black	31.03	24.40	17.91	11.88	8.25	3.00	1.65	0.02	0.70	0.11	0.18	0.29	0.03	0.08	0.05	0.13	0.20	0.05	0.04
S2	23.49	21.43	26.92	9.00	6.63	1.48	9.08	0.02	0.75	0.09	0.15	0.21	0.00	0.06	0.02	0.22	0.36	0.04	0.04
S3	0.00	1.46	89.79	0.00	7.63	0.00	0.53	0.00	0.07	0.00	0.02	0.00	0.00	0.00	0.02	0.04	0.45	0.00	0.01
S4	5.31	30.87	37.54	0.00	11.62	2.76	8.79	0.04	0.98	0.16	0.26	0.34	0.07	0.07	0.03	0.33	0.71	0.08	0.05
S5	43.22	37.68	1.97	9.00	6.05	0.28	0.00	0.00	0.00	0.05	0.54	0.39	0.10	0.55	0.01	0.12	0.01	0.00	0.03
S6-dark red	29.10	30.62	10.36	12.50	11.30	2.60	0.90	0.04	1.16	0.15	0.31	0.40	0.00	0.07	0.02	0.14	0.25	0.06	0.03
S6-red	29.95	30.85	10.54	12.05	10.80	2.90	0.43	0.04	1.10	0.11	0.30	0.39	0.00	0.07	0.03	0.12	0.25	0.07	0.03
S6-green	20.96	15.99	45.54	7.41	5.74	0.60	2.04	0.02	0.48	0.05	0.14	0.21	0.02	0.05	0.01	0.07	0.63	0.04	0.03
S6-black	31.65	21.30	26.66	9.91	5.76	0.65	1.48	0.03	0.70	0.10	0.18	0.25	0.00	0.06	0.02	0.95	0.29	0.04	0.03

presence of SO_3. This can be attributed to the production of sulfate-based compounds as $CaSO_4$, $MgSO_4$, or K_2SO_4 which means there is a partial dissociation of sulfate groups which may give a blackish color as the temperature remains lower around 900–1000 °C. Besides, a carbonaceous compound may also remain on surface or in structure by carbonic acid reactions due to landfill and rain for years [14].

S2 can be seen as pinky white fired mudbrick found in the entrance of gate with S3. As the pinky color established, one can easily understand that there was a clay type raw material that turns to pink by high iron content more than 20 wt% accompanied with high calcium and silicon. Increasing MgO also retards the densification after firing and a sponge-like white + pink color was formed after firing in open air by high oxygen. S2 also has very high amount of SO_3 which has a high capability of compound forming with increased Ca, which also increases the dense firing temperature up to around 1200 °C but a very low degree of dissociation was occurred and the firing temperature remained around 800 °C as indicated by pink color with free iron-oxide content about 21.4 wt%.

S3 is a calcite part which was also collected from the cracks of gate side. There is also firing traces as blackish regions on the part. A low amount of possibly dolomitic structure can be concluded by MgO content. Besides, possibly deposited iron oxide and a very low amount of sulfate former were also found. There was no Si and K containing oxide and even no trace elements were present except SrO, since strontium is another + 2 element of sulfate forming as $SrSO_4$ which is known as celestite and also a very well-known provenance of Sivas mineral ores [14, 15].

In all of these samples, the provenance of the material fits very well with the surrounding structure with high calcium-magnesium-iron containing silicate structure which can be concluded as illite and mixed kaolinite-bentonite with low degree of white color which may mean as secondary moved clays [15, 16]. These clay minerals were not a local formed hydroxide structure, but eroded and moved from long distance by rain or river and collected in a pit of land. The sedimentary and calcite containing mountain structure is known as puzzolanic and gypsum can be grounded to fine size to produce water absorption and get stronger by adding some dried vegetation/litter to produce dried early mudbricks.

S4 in XRF analysis is seen as Ca and Fe reach as well as higher amount of Mg than regular trend. Since there is no known compound of CaO and Fe_2O_3 without intentional phase formation, this oxide amounts can be concluded as separately formed Fe_2O_3 and compound former sulfate for Ca and Mg produces the $CaSO_4$ and $MgSO_4$ within a hydroxide form of $CaMg(OH)_2$/$CaMgCO_3$ which in turn may come from the dolomitic structure of environment and carbonic acid dissolution. The accompanying element oxides such as ferro-silicates and glass forming K_2O may be also due to illitic clay which is responsible from pink-red color with calcium magnesium containing water absorbing clay material [15–17]. As clearly be seen, there are some greenish color around the red and pink colors. This color formation may also due to Mg-Fe-Si oxides named as serpentine/olivine structure which also the mainland provenance soil of Šarišša found in the northern side. This mixed formation can be the proof of an incendiary fire that is not regular and not produced a known shape or phase of materials. The color and formation may give clues about the firing of a pottery or traces of incendiary fire due to some reasons such as war, battle, marauding/plunder, and an accidental fire. Besides main oxides, TiO_2 can be the substitutional of SiO_2 while SrO is same for CaO due to similarity and provenance on Earth.

S5 is a landfill soil rock found right across the left side of the main gate. This rock sample was seen important when we saw greenish fire residuals and color of some samples in green. This was thought to be a good provenance analysis of the mudbricks right before the fire, even after for the formation of same materials and phases if this rock was added to mudbricks by crushing down to powder form as ingredient. After careful analysis, it was seen that this rock sample is a cist/serpentine/olivine rock containing iron oxide as ~ 37 wt%, silicate as ~ 43 wt%, and alumina as 9 wt% along with ~ 6 wt% of MgO and ~ 2 wt% of CaO. The greenish color can come from enstatite or forsterite as Mg-Si oxide with different stoichiometric oxide amounts. Another reason of green color may also come from illitic clay type materials that contain combined oxides with a possible compositional designation of $(Mg, Ca)O.(Fe, Al)_2O_3.SiO_2.nH_2O/nOH$. The differentiating ratios of Mg and Fe with Si oxide may produce green color as known from olivine. As seen from XRF and the mentioned previous fired clay mudbricks, this can easily be seen as the main provenance clay of resultant S2 without any sulfate. Another combination can be a mixture of this rock and $CaSO_4$ in changing weight ratios to produce more puzzolan material. For instance, if one mixes 80 wt% S5 with 20 wt% of S2, then one can produce an S1-black mix which is possible. Within the limits of trace elements, the greenish color may also be attributed to Cr_2O_3 and MnO which are main traces of green glass forming materials even in those amounts [16].

S6 sample was found from the south gate entrance of C building which was subjected to very harsh conditions such as high temperature by seeing reduction formation as slag material and high dissociation due to rain corrosion or wind erosion. XRF analysis of S6 was divided into 4 groups to be identified briefly why the colors are so different by means of elemental and phase compositions. S6-dark red and -red are seen very close by elemental compositions with a slight difference by compound former amount. Sulfate content is twice in dark red one compared to red one which is responsible from $CaSO_4$ formation or low temperature indicator. A slight eye-wise darkness may be due to sulfate containing structure, while other elemental compositions are completely similar as well as trace elements increased up to 1 wt%. Since this material is seen as a slag material with macro bubbles or pores even on surface and inside, it can be concluded that high temperature of about 1200 °C was seen on this material with reductant conditions as closed contact with fire as iron oxide contain increased up to 30 wt% among the fired ones and K_2O was more than usual as 2 wt% that is known as one of the main glass formers in feldspars [16, 17]. An assumption can be done for this material as mixing certain ratios of S5 (70 wt%) with S4 (30 wt%) to produce a similar material as S6-red.

S6-green was seen as yellowish-green in color which may be a slag material with high grinding property even with hand and this may be due to excessive glassification and by presence of high $CaSO_4$ amount. When the clay material containing high Ca and Si meets with water after fire with some reason, the burning and sudden quenching may produce this kind of powder or fluffy sponge sulfate structure due to insufficient calcination. In this manner, high amount of sulfate was calcined but residues remain that may give light greenish color. The firing temperature may be higher than usual but a sudden quenching by rain may produce a fluffy material behind. In the same way, another region with black view is seen with increased Si content which can be also concluded as illitic mixed compounds, almost all are moderate in amount, which can give a blackish output color with some red regions which may also be attributed to iron content. From the trace elements side, ZnO is very unusual that may be a substitutional of CaO and MgO that may also be responsible from matte color and seen as blackish [17].

There may be another proposal for S6 sample since it looked like a slag. As it was found in the far south region of this gate, beyond that gate, which was not excavated further to southeast, there may be a continuing life for blacksmith workers or there may be a workshop as smelting furnace for copper or even a furnace for pottery production. Since the provenance analysis makes the production of mudbricks in here around, there may be some important pottery makers around who need to fire those. The earlier findings can say some provenance possibilities to us that there must be a service industry for continuing of the in-castle life even for bringing water from the very well-known dam. There may be an approximation to the population of Šariššа about more than 1000 people who may need many pottery products as well as places to fire them to use simultaneously.

Scanning electron microscopy-energy dispersive spectroscopy (EDX) analysis

As seen from Fig. 3, in low magnification, there are evidence of partial sintering of red/black color of S1 sample. Especially the bubbles as well as pores are also seen, this may mean that the vitrification takes place during the fire by the aid of K and Na as main glassifiers [18–20]. Sp1 is the areal quantification which relies as an abundant ratio of all elements in the image. The fired sample is seen in contact with natural environment due to open pores and among the interconnected pores, there are some isolated closed pores [19, 20].

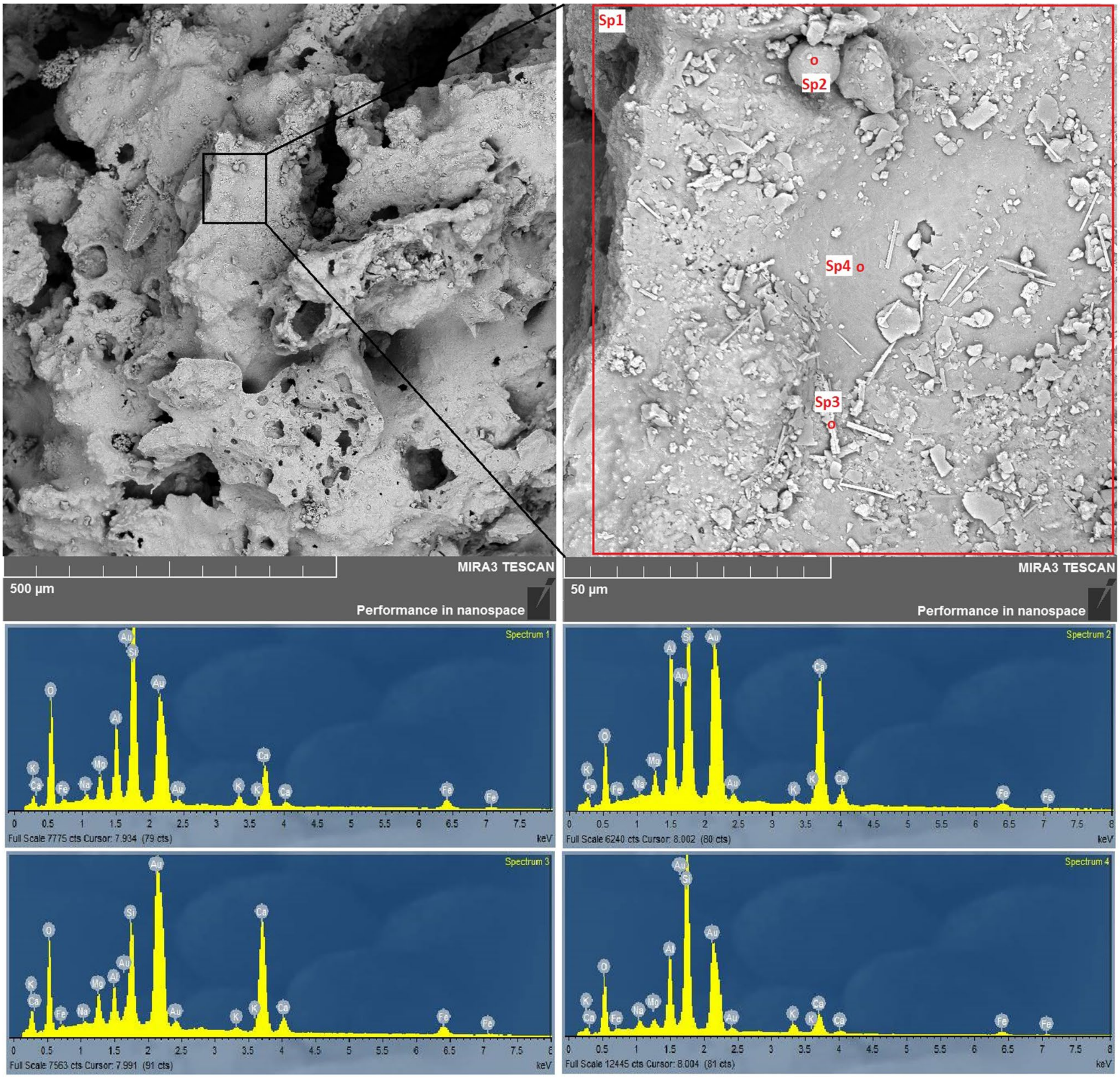
As in high magnification image on the right, the presence of spheroid structures that contain high Ca and Si content as well as Al with other accompanying elements may be the proof of anorthite/gismondine/gehlenite structures that come from a Ca rich clay mineral of illite/muscovite type as in Sp2 [20–22]. The need-like structures can be concluded as Ca rich ferrosilicate with high Mg and low Al content in Sp3. $CaO.MgO(Fe,Al)_2O_3.SiO_2$ can be said as another high temperature phase of illite that subjected to phase separation. Sp4 remains as the smoothest sintered surface which consists of high Na and K as glassifiers and high in Al and Si but low in Ca and Fe. This phase was separated from the other Ca-Fe rich content as this can be called as cyanite/sillimanite that produces the glass phase and binding ability [19–22].

SEM image of sample 2 is seen in Fig. 4. The fractured surface is seen as agglomerated very thin particles of Ca rich oxides with very low amount of Si-Al–Mg and Fe that makes the sample $CaO/CaSO_4$ rich calcite/gypsum formation. As clearly seen, there is a high contact possibility of water with the structure that produces $CaCO_3$ and gypsum hydrate structure. The carbonic acid content of soil or even after rain, the alteration becomes more aggressive and hydration is in progress by years, and the increased Ca content gives rise to elemental dissociation from the structure that was subjected to low sintering temperature of 800–900 °C.

As in Sp1, the main phase is CaO which was altered with carbonic acid and possible the form of $CaCO_3$ as found from quantification. Since S is in the lowest state, carbonate species may be dominant. As Sp2 and Sp3 were investigated, S becomes more dominant and $CaSO_4$ with hydrate type forms. Since Si, Al, and Fe are as low as trace, these particles are a mixture of $CaO/CaCO_3/CaSO_4$ in hydrated forms.

By Sp4 areal quant, the average of all three points is seen that means the regular distribution of pink clay by iron content is evident with high amount of calcite-carbonate and sulfate phases.

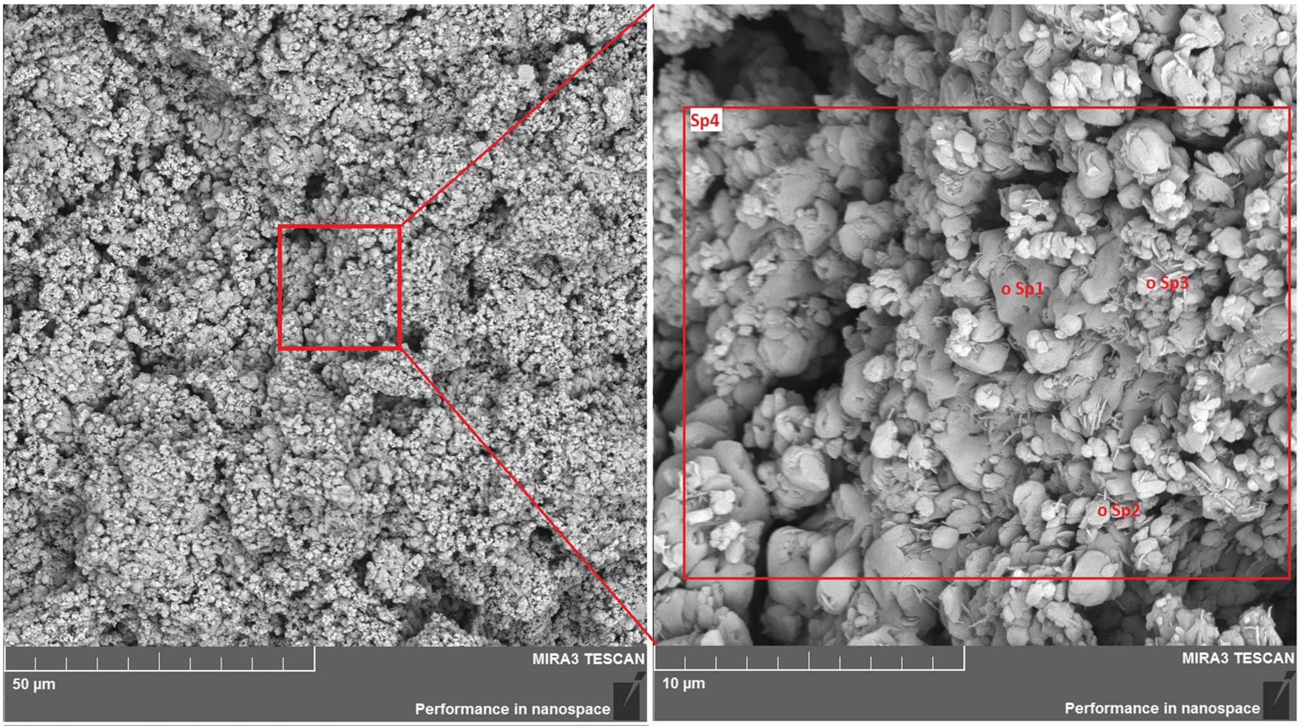
S3 is seen in Fig. 5 with the highest calcium containing sample. The sample was investigated from top and bottom side due to carbonization traces. SEM image of top side is seen as fine powdered calcium carbonate formation with

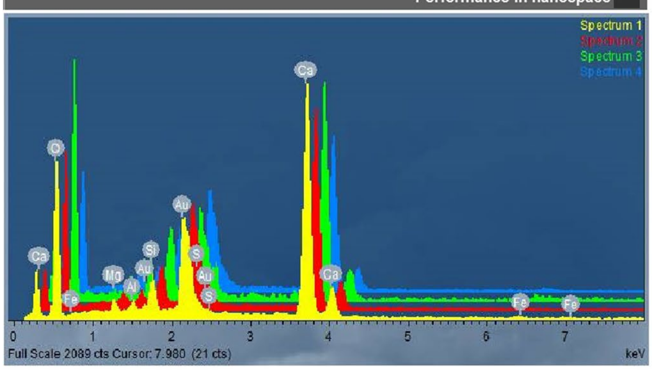


Spectrum	O	Na	Mg	Al	Si	K	Ca	Fe	Total
Spectrum 1	47.30	1.02	2.93	7.70	23.31	1.87	9.22	6.65	100.00
Spectrum 2	35.10	0.26	2.24	11.88	21.71	0.63	24.89	3.29	100.00
Spectrum 3	50.54	0.41	3.59	3.95	10.63	0.65	23.76	6.47	100.00
Spectrum 4	40.94	1.72	1.42	10.53	31.78	2.85	7.03	3.74	100.00
Mean	43.47	0.85	2.54	8.52	21.86	1.50	16.22	5.04	100.00
Std. deviation	6.86	0.66	0.93	3.51	8.69	1.07	9.41	1.77	
Max.	50.54	1.72	3.59	11.88	31.78	2.85	24.89	6.65	
Min.	35.10	0.26	1.42	3.95	10.63	0.63	7.03	3.29	

Fig. 3 SEM image of sample 1 at low magnification in upper left; high magnification of small black rectangle in upper right, corresponding EDX spectrums and quantification results

low water adsorption or contact characteristics. Generally, there is high content of Ca which is around 55 wt% for Sp1 which is close to stoichiometric CaO ratio. Sp2–3 as well as Sp4 as average give information about the calcium carbonate structure with low water intake. The





Spectrum	O	Mg	Al	Si	S	Ca	Fe	Total
Spectrum 1	62.11	1.03	0.62	2.49	0.89	31.97	0.90	100.00
Spectrum 2	63.26	0.78	0.87	2.61	2.46	29.62	0.40	100.00
Spectrum 3	65.11	0.98	1.94	3.63	2.86	24.36	1.14	100.00
Spectrum 4	60.71	1.42	1.53	4.86	1.88	28.51	1.09	100.00
Mean	62.80	1.05	1.24	3.39	2.02	28.61	0.88	
Std. dev	1.86	0.27	0.60	1.10	0.85	3.18	0.34	
Max.	65.11	1.42	1.94	4.86	2.86	31.97	1.14	
Min.	60.71	0.78	0.62	2.49	0.89	24.36	0.40	

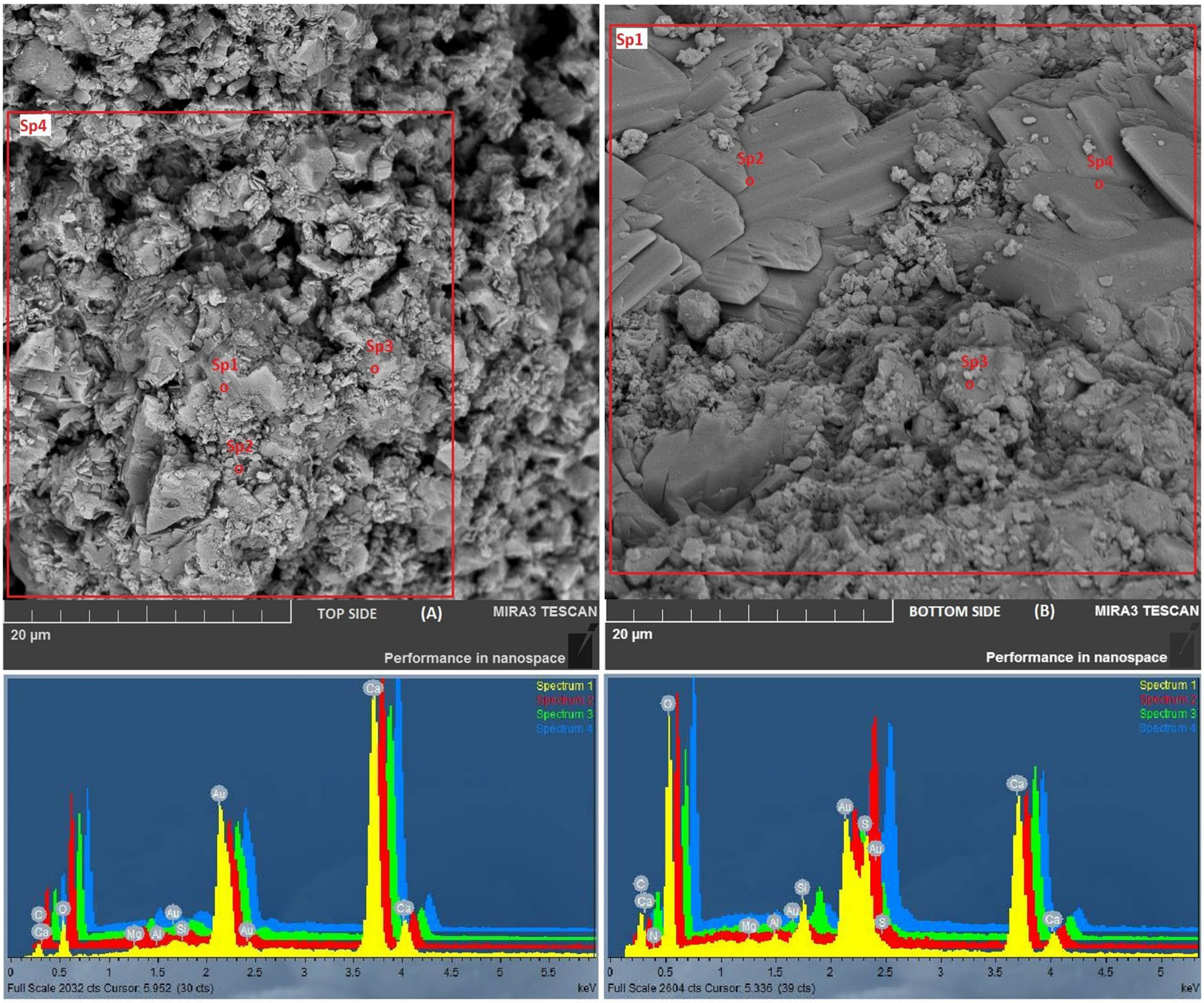
Fig. 4 SEM images of sample 2 and corresponding EDX spectrums and quantification results

stoichiometric amount of Ca in $CaCO_3$ is around 40 wt% which is deteriorated by other trace element entrance to body.

SEM image from the bottom of sample is seen on the right. The elemental configuration was completely changed due to water and sulfate absorption and dissociation by soil ingredients. Volatile compounds as C, S, O, and N increased, so the Ca rich many phases can form by dissolution precipitation process that is in progress by the presence or absence of water. Sp1 is the average amounts of ingredients with volatiles precipitated from water. By Sp2 and Sp4 quant, the longitudinal grown plaques are seen as $CaSO_4$-$Ca(NO_3)_2$-$CaCO_3$ mixture, grown such a mixed salt precipitation. Sp3 is also seen as sulfate rich region by small precipitates since sulfates have low solubility in water.

SEM images (low mag. on the left, high mag. on the right) and corresponding EDX quantification are seen in Fig. 6. There are many different regions due to the firing condition and temperature are seen. The Ca containing illitic clay was separated to different phases either by water input after fire or at the extinguishing stage of fire, or due to the differentiation of elemental composition in some region by irregular distribution.

As in quant results, Sp1 is seen as Ca–Si rich clay with Fe, K, and Mg ingredients as a regular illitic/muscovite type clay with high carbonaceous material. Sp1 contains elongated anorthite-like structures; between them, clay was filled. Sp2 is also Ca containing but limited to 4 wt% which seems to be altered by water intake and precipitated from water as very fine interconnected particles. Among them, $CaCO_3$ self-grown particle with hexagonal longitudinal c axis morphology was seen in Sp3 and in high mag. SEM



Spectrum	C	O	Mg	Al	Si	Ca	Total
Spectrum 1	5.84	37.80	0.45	0.01	0.49	55.41	100.00
Spectrum 2	12.89	55.36	0.65	0.21	0.26	30.64	100.00
Spectrum 3	12.68	54.76	0.79	0.19	0.39	31.19	100.00
Spectrum 4	13.05	54.37	0.75	0.17	0.37	31.29	100.00
Mean	11.11	50.57	0.66	0.14	0.38	37.13	100.00
Std. deviation	3.52	8.52	0.15	0.09	0.09	12.19	
Max.	13.05	55.36	0.79	0.21	0.49	55.41	
Min.	5.84	37.80	0.45	0.01	0.26	30.64	

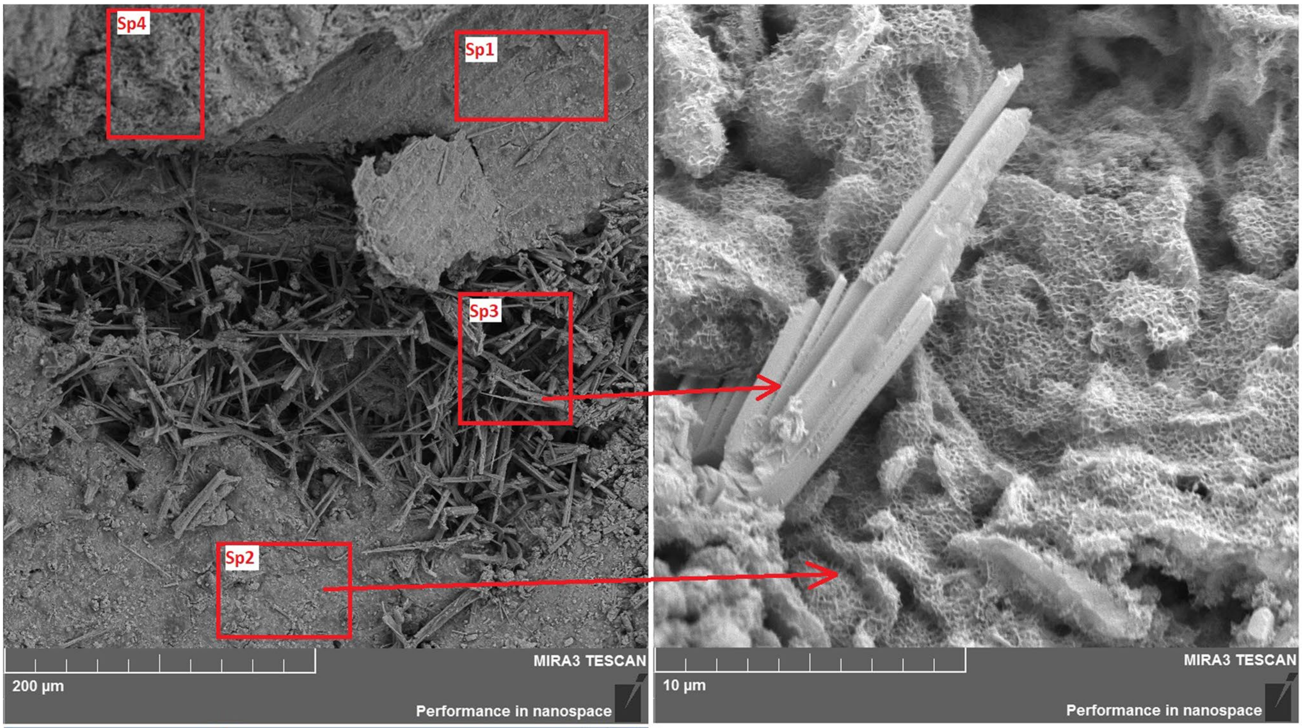
Spectrum	C	N	O	Mg	Al	Si	S	Ca	Total
Spectrum 1	12.61	5.60	57.68	0.24	0.35	1.83	6.58	15.11	100.00
Spectrum 2	9.42	5.03	58.13	0.00	0.06	0.33	12.80	14.23	100.00
Spectrum 3	13.43	6.15	56.23	0.23	0.37	2.07	3.30	18.22	100.00
Spectrum 4	8.91	4.74	60.48	0.08	0.22	0.51	11.19	13.87	100.00
Mean	11.09	5.38	58.13	0.14	0.25	1.19	8.47	15.36	
Std. Dev.	1.96	0.54	1.53	0.10	0.12	0.77	3.76	1.71	
Max	13.43	6.15	60.48	0.24	0.37	2.07	12.80	18.22	
Min	8.91	4.74	56.23	0.08	0.06	0.33	3.30	13.87	

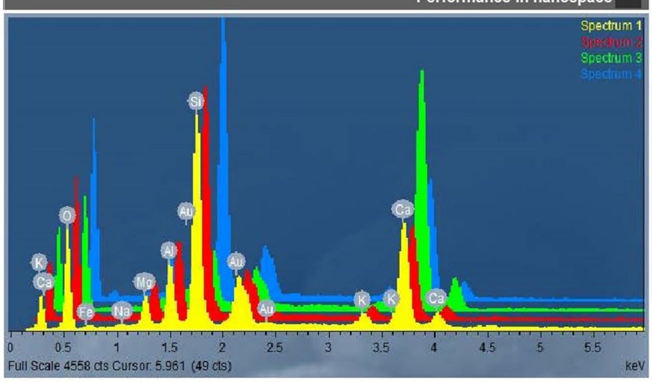
Fig. 5 SEM images of sample 3 and EDX compared spectrums and quantification results of **A** top side and **B** bottom side of sample

image on the right. In Sp3 quant, Ca increases up to 25 wt% while others disappear. Sp4 is the highest sintered area even before extinguishing possibility, since Ca decreases to regular amount of 12 wt% while Al, Fe, Mg, and Si come normal levels of illitic clay, oxygen is increased to expected amount while C drastically decreased.

SEM and EDX analysis of sample 5 are seen in Fig. 7. As a very well-known rock type, this stone piece can be concluded as olivine/serpentine group of one of the most provenance rock types in Sivas especially in Altinyayla-Kuşakli region of Sivas. As evident from SEM images, this rock is fully dense and pore free even inside the rock and consists of mainly Mg-Si oxide which can be attributed to olivine structure in metamorphic structure contacted with calcite regions. A moderate wt% amount of Fe is evident with very low Ca as in general Sp1 areal quant as well as Sp2 and Sp4.

There is a discrepancy in Sp3 as Fe content was huge. As seen in SEM high mag. image, whiter regions indicate the heavier element concentration; in this case, this is iron. While others were drastically decreased, Fe content





Spectrum	C	O	Na	Mg	Al	Si	K	Ca	Fe	Total
Spectrum 1	24.36	35.09	0.07	1.83	3.30	12.96	1.26	13.05	8.07	100.00
Spectrum 2	29.54	39.58	0.04	1.82	3.30	11.06	1.00	9.59	4.07	100.00
Spectrum 3	26.69	42.22	0.03	0.47	0.75	2.59	0.45	25.11	1.69	100.00
Spectrum 4	13.72	46.33	0.18	2.04	4.09	14.66	0.96	12.78	5.25	100.00
Mean	23.58	40.80	0.08	1.54	2.86	10.32	0.92	15.13	4.77	100.00
Std. dev.	6.90	4.71	0.07	0.72	1.46	5.35	0.34	6.83	2.65	
Max.	29.54	46.33	0.18	2.04	4.09	14.66	1.26	25.11	8.07	
Min.	13.72	35.09	0.03	0.47	0.75	2.59	0.45	9.59	1.69	

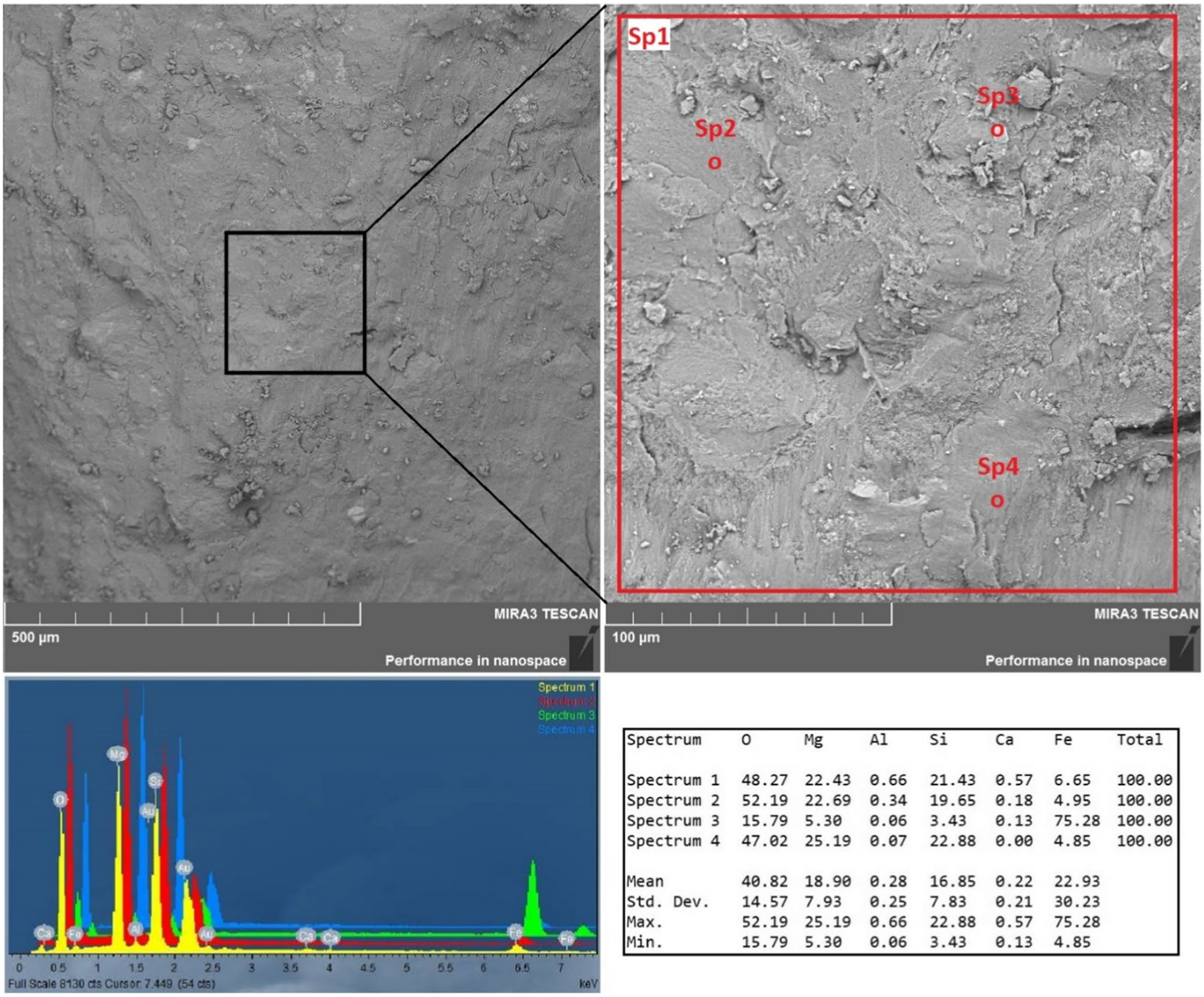
Fig. 6 SEM low mag. on the left and high mag. of sample 4 on the right and their EDX spect. and quant

increases up to 75 wt% which means this region is an iron agglomeration region with phase separation in metamorphism period. There are some other spots that color was differentiated which are also Fe regions.

As continuing of Fig. 7, this provenance rock formation can be a good proof of green regions in fired rocks as the mudbricks can be most probably to be produced in this region. By mixing the powders of this rock type material with other clays as well as an active puzzolanic material such as calcium sulfate hydrate, the mudbricks with litter addition can be produced easily. As a proposal, there can be also a workshop or furnace to fire potteries to be used but not excavated yet, which may be due to some surficial provenance of pottery pieces on the ground and even after early excavations.

Another high temperature fired slag piece or incendiary part of mudbricks was seen as sample 6 in Fig. 8. The outer region was seen in Fig. 8A while inner side can be seen in Fig. 8B as well as their EDX analysis, respectively.

The outer region is seen as Fe rich in all quantified spots with a newly accompanying element of Cu. Since Cu is the main transition element of 13th BCE, the trace "first time" finding is very important. The reduction, if thought, is very low for Fe but increased the iron content of clay or other material may be from 15–20 up to 30–37 wt% for the upper quant results with accompanying low amount of Cu residue and/or trapped Cu in slag which is seen in the pyrometallurgical process of Cu, earlier. Especially in Sp2, Cu content was increased up to 1.1 wt% with Ti content suddenly up to 6.5 wt% while others were decreased. This may be due to



Spectrum	O	Mg	Al	Si	Ca	Fe	Total
Spectrum 1	48.27	22.43	0.66	21.43	0.57	6.65	100.00
Spectrum 2	52.19	22.69	0.34	19.65	0.18	4.95	100.00
Spectrum 3	15.79	5.30	0.06	3.43	0.13	75.28	100.00
Spectrum 4	47.02	25.19	0.07	22.88	0.00	4.85	100.00
Mean	40.82	18.90	0.28	16.85	0.22	22.93	
Std. Dev.	14.57	7.93	0.25	7.83	0.21	30.23	
Max.	52.19	25.19	0.66	22.88	0.57	75.28	
Min.	15.79	5.30	0.06	3.43	0.13	4.85	

Fig. 7 SEM low mag. of sample 5 on the left and high mag. on the right and their EDX spectrum and quant results

K and Ca increase favored the phase separation of Ti and Cu and resulted in precipitation even in firing temperature of more than 1200 °C followed by sudden cooling or after incendiary of mudbrick with reducing atmosphere by surrounding fired bricks.

In the inner part as seen by Fig. 8B and its quant, the SEM image shows pores and low viscosity glass formation due to high temperature as Na and K as main glassifiers are present especially in Sp1 and Sp2. In Sp1, the phase can be identified as (Ca, Fe)SiO_3 or $CaFe_2SiO_6$ as fayalite-like structures with Ca content and high density, while Sp2 can be concluded as an illitic Na containing glass material with expected amounts of Fe, Ca, K, and Al with absence of Mg.

The presence of low amount of C can be said as reduction possibility of something such as litter in mudbrick which remained in without evaporation by sudden glass formation but left the material later by bubble production by low viscosity and left some residue even in the mudbrick. As in Fig. 8B', Sp3 is seen as iron increased inside the separated square-like particles surrounded by glass which in turn can be the source of outer Fe increase that come by bubbles to form pores inside. Sp4 is a total SiO_2, free quartz surface without any other principal oxides, even Fe is as low as 2 wt% and others are trace as lower than 1 wt%.

Conclusions

The importance of Šarišša is very well-known in archeological field and the city is one of the most important and biggest cities of Hittite Empire in the middle Anatolian city in Sivas. By this provenance study and brief discussions on XRF and SEM–EDX analysis, following conclusions can be derived:

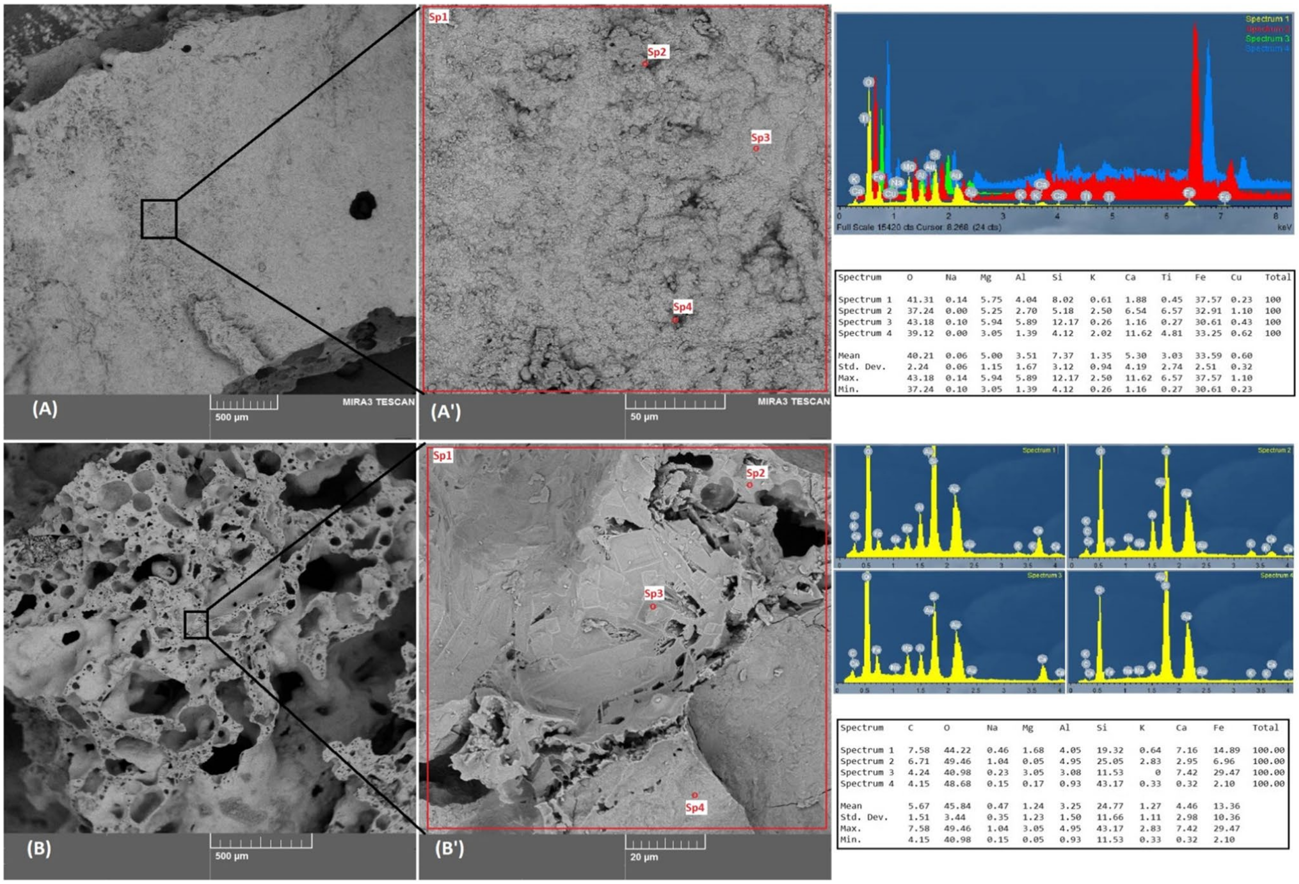


Fig. 8 SEM photos of sample 6. **A** for outer; **A'** high mag. and EDX spect. and quant on upper right; **B** for inner; **B'** high mag. and EDX spect. and quant on lower right

- The main construction material is mudbrick of different clay minerals and puzzolans such as calcium carbonate and/or calcium sulfate (gypsum) mineral of Sivas's regular provenance.
- It is still unknown if there is a workshop for pottery production as well as furnaces for firing them to be used by public. There are known two main stratigraphy as Hittites and Roman Empire. Almost all mudbricks were fired in some reason either by incendiary firing or due to a battle.
- A brief XRF analysis was evaluated on six samples collected from the castle and temple region of Šariššа. XRF studies showed that fired samples were Ca rich clay minerals mostly, with different firing temperatures as well as slag type materials were also found. From pure mudbricks to high temperature fired mudbricks even in reduced state were also evident.
- SEM–EDX analysis was also briefly discussed for samples of interest and temperature difference was seen by sintering types. Glassification occurs in low Fe, Ca containing oxides while Na and K were high as glass forming agent oxides. The pores are produced by vitrification and viscosity decrease as melting like structures with bubbling possibility. The glass wall effect is very evident as well as phase separation regions either Ca or Fe rich phases. The alteration is also a very well-known situation that Ca containing carbonate and sulfate rich materials have water intake due to rains for years and soil contact. The precipitation of phases is due to the soil contact and water adsorption was seen by dissolution–precipitation studies.
- Since 2005–2006 seasons, there was no regular excavations on site, and this is a handicap for the conservation of place due to no-closed region was made and wind-rain and snow possibility by the regular weather conditions of icy to windy rain. These weather conditions make the samples erode and deform to high extent. There should be a conservation plan for Šariššа to prevent the deterioration of area as well as the protection of cultural tourism to be re-entertained. Future studies are still planned for these purposes and new provenance studies were carried out by XRF, SEM–EDX analysis. The permissions will also be taken for new studies and a new excavation team should be re-established for replenishing the area.

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