



Micro-Raman and FT-IR spectroscopic studies of ceramic shards excavated from ancient Stratonikeia city at Eskihisar village in West–South Turkey



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ABSTRACT

In this study, micro-Raman and Fourier transformed infrared (FT-IR) spectroscopies, X-ray diffraction (XRD) and scanning electron microscope with energy dispersive X-ray (SEM-EDX) were used to characterize the mineralogical structures of pigments of four ceramic fragments in which one of them belongs to Hellenistic period (1st – IVth century BC) and other three ceramic shards belong to Early Rome (IVth century BC– 1st century AD) excavated from Stratonikeia ancient city. In the results of investigations on these four ceramic fragments, the various phases were identified: quartz, kaolinite, albit (or Na-feldspar), calcite, anastase, hematite and magnetite. Furthermore, the obtained findings indicate that firing temperature is about 800–850 °C for all the shards.

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1. Introduction

Ancient Stratonikeia city is located at Eskihisar village of Yatağan town of Muğla province in West–South Turkey (Fig. 1). Although the first settle downs in this region became in the period of Bronze Age, the archaeological finds belong to the end of 2000 BC [1]. Stratonikeia was founded at the beginning of Hellenistic period by the Seleucid King, Antikhos the first in the honor his wife Stratonike.

The first excavations in the mentioned archaeological site were verified by Prof. Yusuf Baysal and his team in 1977. However, the artifacts have been excavated under the auspices of Pamukkale University, Turkey, since 2008.

It is well-known that the analysis of the archaeological remains is quite important in order to obtain the maximum amount of information on an object for the archaeologists. Therefore, an interdisciplinary approach is asked for the analysis of pigments, clay,

structures and mineralogical characterization of ancient ceramic fragments. Micro-Raman spectroscopy is a powerful non-destructive analytical method on ceramics, paintings, mummies and various ancient objects [2–8]. On the other hand, FT-IR spectroscopy as the complement of Raman spectroscopy provides useful information about the firing temperature performed for the production of ceramics [9–12]. Other two complementary methods can be considered as SEM-EDX and X-ray diffraction (XRD) on ceramics [13,14].

The purpose of this study is to present for the first time the results of IR and micro-Raman spectra of four ancient ceramic shards by considering data obtained from XRD and SEM-EDX measurements.

2. Experimental

2.1. Sample preparation

The ceramic fragments excavated from the archaeological sites were cleaned by conventional method. First, they are cleaning by using a brush under water without giving any damage to artifacts and then, were dried in air at room temperature. The specimens studied are described in Table 1.

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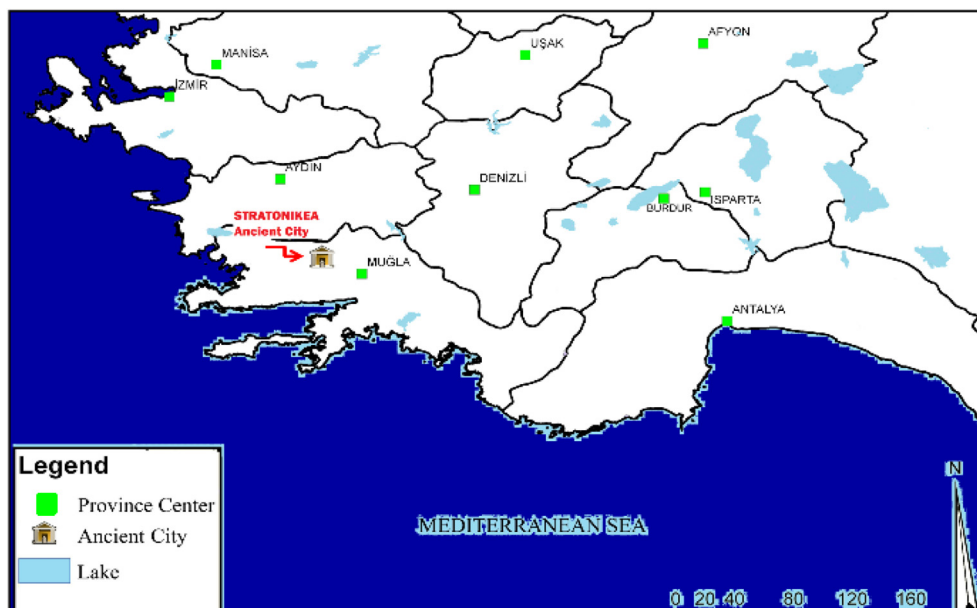


Fig. 1. The location of ancient Stratonikeia city in South–West Turkey (map with Assoc. Prof. Kadir Temuçin's courtesy).

Table 1
Data on ancient ceramic fragments.

Sample labeling	Description
STR-1	A shard of a large bowl (ca. IVth – 1st century BC. in Hellenistic period) excavated from ancient Stratonikeia city. STR-1a and STR-1b denote bright red and pale red regions on the outer side of the shard, respectively and STR-1c indicates a region on inner side of the mentioned shard.
STR-2	A shard of a plate excavated from Stratonikeia city (ca. IVth century B.C–1st century A.D in early Roman period). STR-2a and STR-2b show dark red and brownish yellow regions on the outer side, respectively, and STR-2c denotes dark brown region on the inner side of the shard.
STR-3	A fragment of a plate excavated from Stratonikeia (ca. IVth century B.C–1st century A.D in early Roman period). Outer side is from pale red (STR-3a) and dark brown coating (STR-3b). Inner side is dark brown coating (STR-3c).
STR-4	A fragment of a plate excavated from Stratonikeia (ca. IVth century BC –1st century A.D in early Roman period.). Outer side is dark brown coating (STR-4a) and inner side is black coating (STR-4b).

The photographs of analyzed samples are shown in Fig. 2. In these photographs the labeled circles show the parts of the ceramic shards from where the measurements are verified.

2.2. Instruments

2.2.1. X-ray diffractometer

XRD patterns were recorded using a X'Pert PRO (PW 3040/60 Model) powder diffractometer with CuK α (1.54060 Å, 40 mA, 45 kV) at 0.02 steps at the rate of 0.5 per second over range $5 < 2\theta < 75$.

2.2.2. Scanning electron microscope (SEM)

The SEM images and energy dispersive X-ray (EDX) graphics of

the pigments on the surfaces of ceramic shards studied in this work were monitored by VEGA-II LSU Variable Pressure Scanning Electron Microscope.

2.2.3. Micro (μ) –Raman spectroscopy

Micro-Raman spectra of the samples were recorded at room temperature using a Jasco NRS-3100 Laser Raman Spectrometer equipped with the CCD detector cooled at -50 °C. The excitation source was a diode laser, operating at 785 nm and scan number was 10.

2.2.4. Infrared spectroscopy

The samples were compressed into self-supporting pellets and introduced into an IR cell equipped with KBr windows. IR measurements at room temperature were performed on a Perkin–Elmer Spectrum One FT-IR (Fourier Transformed Infrared) Spectrometer with a resolution of 4 cm $^{-1}$ in the transmission mode.

3. Results and discussion

3.1. XRD patterns

XRD analysis provides the recognition of the mineral characterization of ceramic potteries and the composition of the crystallographic phases which are related to their provenance [15]. XRD patterns of the specimens which are described in Table 1 and shown in Fig. 2 are listed in Table 2.

As seen in Table 2, the existence of quartz (α -SiO $_2$) mineral is available for all of the samples. However, for the ceramic shard STR-1 the major primary mineral present in the sample is kaolinite [Al $_2$ Si $_2$ O $_5$ (OH) $_5$] and the secondary mineral present is quartz and the accessory minerals present in the sample are the biotite which is a mica group mineral at the approximate chemical formula [K(Mg,Fe) $_3$ AlSi $_3$ O $_{10}$ (F,OH) $_2$] and gypsum [CaSO $_4$.2H $_2$ O].

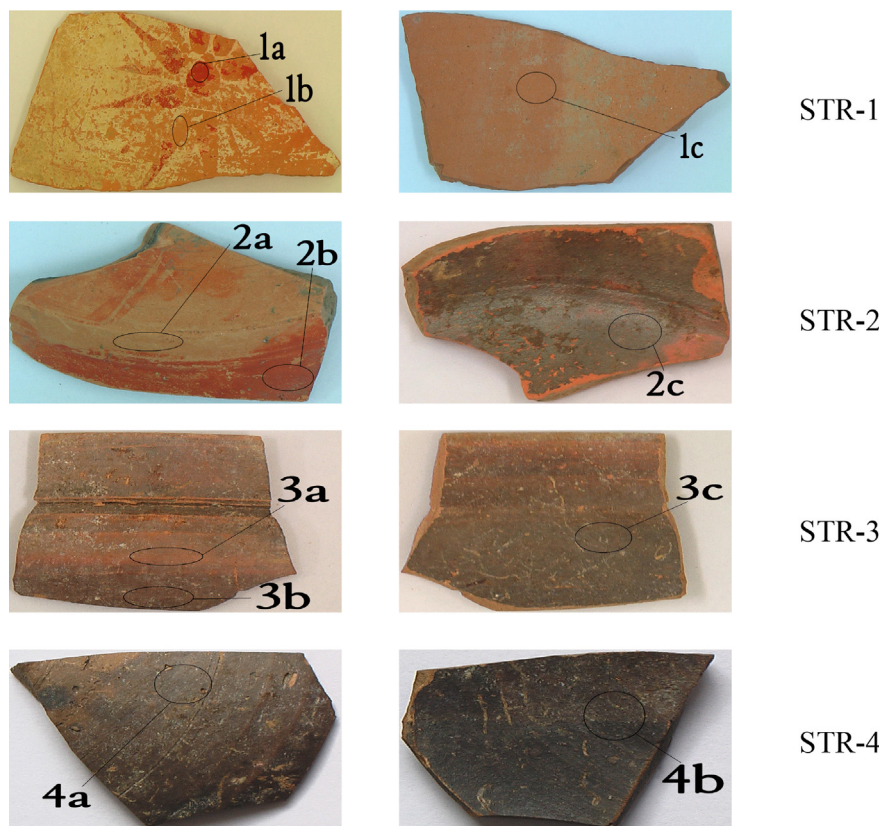


Fig. 2. The photographs of analyzed STR-1, STR-2, STR-3 and STR-4 samples (their inner sides on the left and outer sides on the right.).

Table 2
Mineral phases of the specimens.

Specimens	Minerals
STR-1a	Quartz, Calcite, Kaolinite, Biotite
STR-1b	Quartz, Biotite, Kaolinite, Gypsum
STR-1c	Calcite, Quartz, Albite
STR-2a	Quartz, Biotite
STR-2b	Quartz, Illite
STR-2c	not detected
STR-3a	Quartz, Albite, Calcite
STR-3b	Quartz, Hematite, Albite, Calcite
STR-3c	Quartz, Hematite
STR-4a	Quartz, Albite
STR-4b	Quartz, Albite

Furthermore for the other sample the minerals present are albite [NaAlSi₃O₈], calcite [CaCO₃], hematite [α -Fe₂O₃] and illite [KAl₄(-Si₇AlO₂₀)(OH)₄].

3.2. SEM-EDX elemental analysis

Scanning electron microscope with energy-dispersive X-ray (SEM-EDX) microanalysis is used to obtain elemental composition of the ceramic shards and also fitted with an image for each sample [16]. For the sake of convenience, the XRD pattern, EDX analysis and SEM image for only the St-1A shard part are given in Fig. 3(a), (b) and (c), respectively. The SEM-EDX analyses of four samples

confirm the existences of the Si (with high concentration), Al, Fe, Ca, Mg, Ti, K, P and Na elements. By considering the results of SEM-EDX analyses, the main elements existed in the ceramic shards are listed in Table 3.

3.3. Micro-Raman and FT-IR spectra

The micro-Raman and FT-IR spectra of the ceramic shards St-1 St-2, St-3 and St-4 are shown in Fig. 4(a) and (b), respectively. By considering the micro-Raman and FT-IR spectra of all shards in this study, the characteristic Raman and infrared frequencies for the identified minerals are given in Table 4 and in Table 5 with the references numbers which are obtained from different sources, respectively. However the frequency values for the identified minerals of the mentioned parts for each ceramic shard can be shifted at the interval of 2–8 cm⁻¹ as seen in Table 4.

Since the horizontal scales of the graphics are almost same in Fig. 4(a) and (b) spectra, some representative wavenumber values are shown for only on the top vibrational spectra.

Furthermore, the characteristic micro-Raman and infrared wavenumber assignments of the ceramic shards labeled St-1, St-2, St-3 and St-4 are listed in Tables 4 and 5, respectively, as well as their relevant sources.

As seen in Table 4, the micro-Raman frequencies of hematite for all of the shards which exhibit highly small shifts are in a very good agreement with values in the previous reported works [17–20]. The

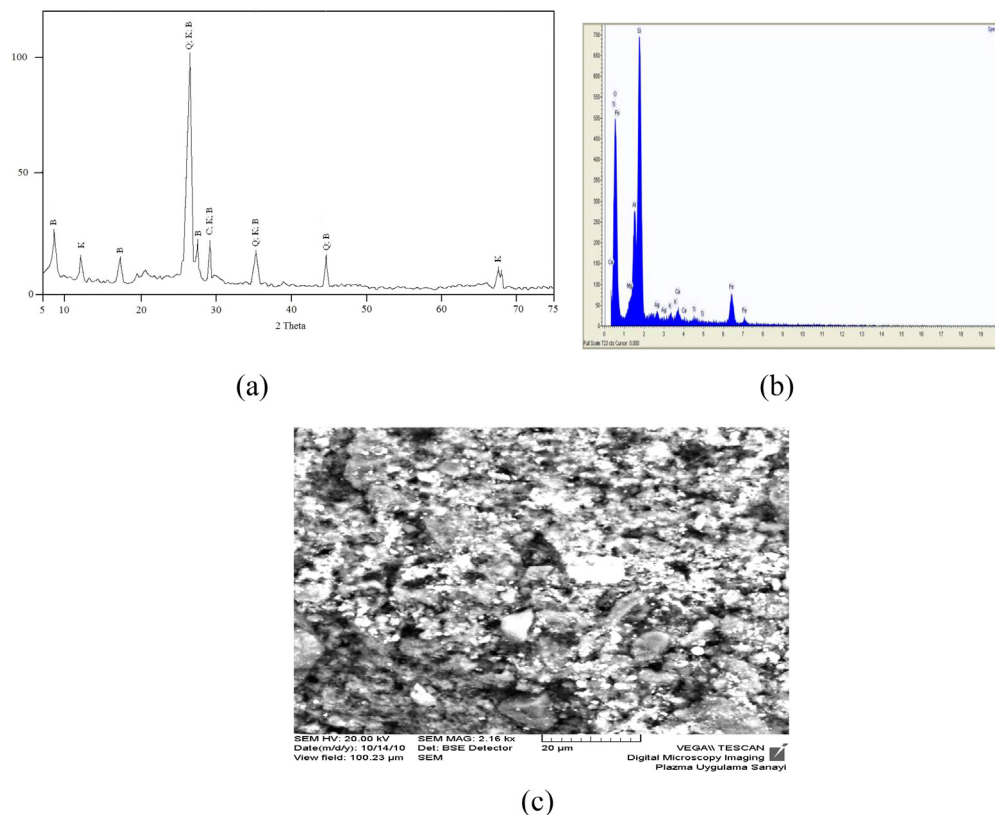


Fig. 3. (a) The XRD pattern, (b) EDX analysis and (c) SEM image for the St-1A shard part. (The capital letters on XRD pattern and EDX graphics denote the phases described in Table 2.)

Table 3
SEM-EDX elemental analysis results of samples (%).

Samples	Al	Si	Fe	Ti	Ca	K	Mg	P	Na
STR-1a	8.22	23.89	7.17	0.29	1.02		1.39	0.54	
STR-1b	12.07	19.66	6.47	0.63	1.32		1.54	0.19	0.13
STR-1c	12.96	24.67	3.39	0.54	4.32	2.65	0.39		
STR-2a	11.78	18.76	2.85	0.4	1.35	0.70	1.46		0.47
STR-2b	12.70	16.89	2.73	0.39	0.80	1.69	2.32		0.67
STR-2c	13.17	11.33	2.62	0.43	0.34	0.75	1.09		0.96
STR-3a	11.73	20.99	7.78	0.27	1.84	2.95	0.64	0.67	
STR-3b	8.06	18.38	4.33	0.31	5.95	1.78	0.75	2.35	3.55
STR-3c	9.87	21.78	6.04	0.46	2.86	2.35	0.50	1.26	1.17
STR-4a	3.34	10.64	2.03	0.17	19.32	0.92		9.13	
STR-4b	8.99	26.61	2.51	0.29	1.47	2.36			

Raman spectroscopic analysis of the samples shows the presence of hematite which is one of the most intense coloring materials since it includes relatively high iron oxide which is confirmed by XRD and SEM-EDX results. Similarly, the micro-Raman frequency values of other minerals are also in good agreement with the previous works [17–30].

In Table 5, the assignments have been made on the ground of the characteristic infrared frequencies of the minerals [24,31–34]. By considering Fig. 4(b) and Table 5, the infrared peaks of calcite in all the shards are observed as strong bands at 612–616 and 876 cm^{-1} and as strong and broad bands at the interval 1428–1459 cm^{-1} [32]. Likewise, the infrared vibrational frequency

values of quartz, hematite, kaolinite, albite and amorphous carbon are also in good agreement with values existed in the literature [18,24,31–34].

Furthermore, the main Si–O stretching vibrational bands were deduced at the intervals 1038–1043 cm^{-1} for kaolinite and 1069–1078 cm^{-1} for quartz in all ceramic shards. According to Shoval and coworker the Si–O stretching band can be slightly shifted to the higher wavenumber [9]. At the same time, it is well-known that the estimation of firing temperature of ancient ceramics can be obtained from infrared spectroscopy [11]. On the other hand, the Al–OH stretching peaks were not detected for the mentioned shards as seen in Fig. 4(b). In this framework, we can state that the firing temperature of the samples is about 800–850 °C.

4. Conclusion

In conclusion, we can state that the existences of hematite, magnetite, quartz and albite for the shards under study are identified by considering the obtained results from the combination of vibrational spectroscopies, the XRD and SEM techniques which have a large application area in the archaeological researches. The infrared results supported with other techniques suggest that the firing temperatures of the labeled St-1, St-2, St-3 and St-4 ceramic shards are about 800–850 °C and the existence of hematite indicates the firing in an oxidizing atmosphere.

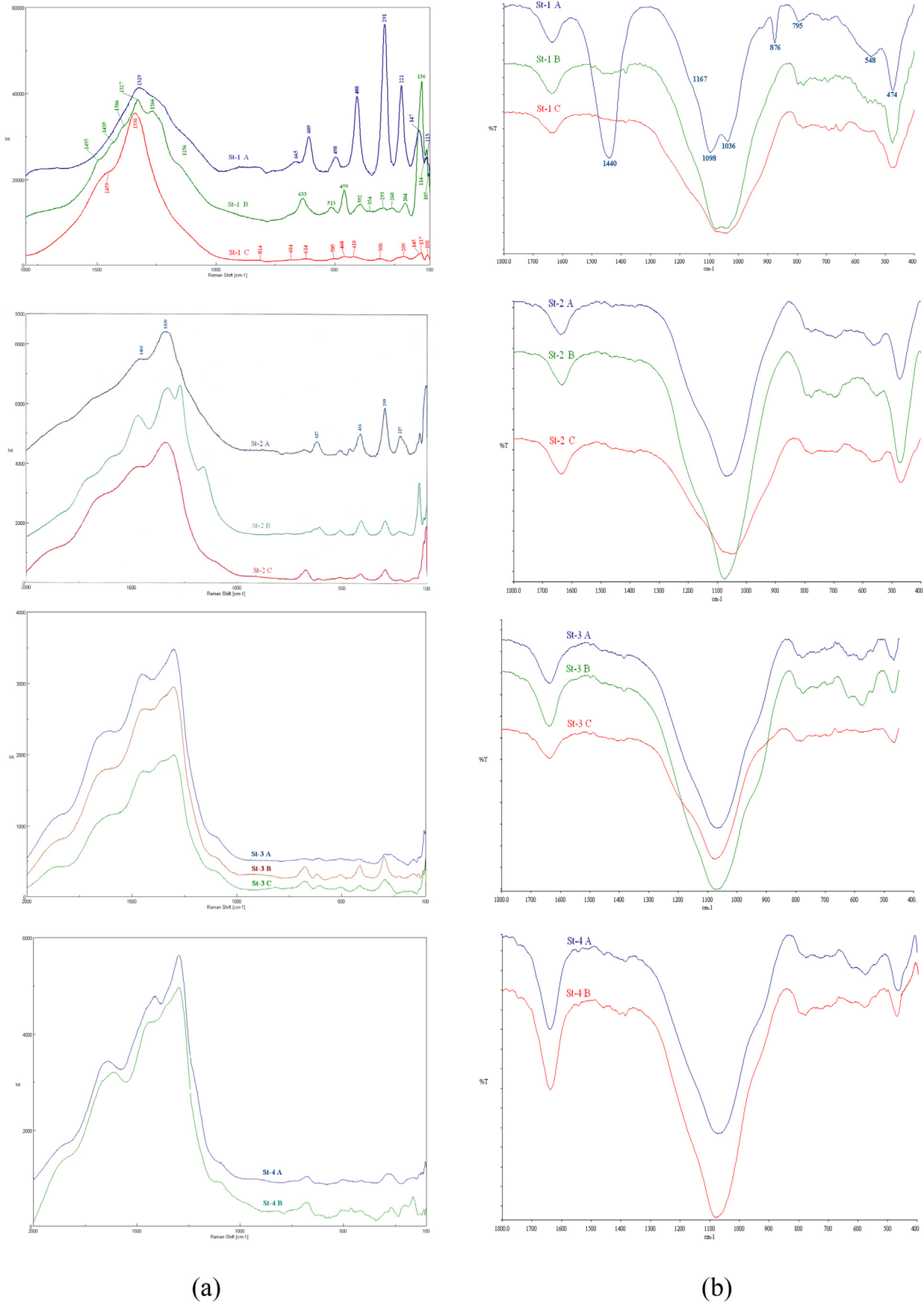


Fig. 4. Micro-Raman (a) and IR (b) spectra of St-1, St-2, St-3 and St-4 ceramic shards.

Table 4

The characteristic micro-Raman wavenumbers for the minerals possibly existed in the mentioned ceramic shards. The relevant sources have been reported within the brackets in the first column.

Minerals	Raman wavenumbers (cm ⁻¹)
Hematite [17–20]	220, 222, 224–226, 245,291–294, 406, 410–411, 496, 608–609,611–612, 614, 1296, 1302–1303, 1307, 1319,1327–1328, 1330–1333,
Magnetite [18]	298, 299, 665,
Maghemite [18]	672, 674, 672, 677, 678
Quartz [20,21]	460, 462,464, 467, 468, 810, 1086, 1089, 1090, 1163
Calcite [17,19]	156, 1418, 1432, 1435
Anatase [19,22,30]	142, 144, 394, 510, 511, 513, 635
Kaolinite [23,24]	132, 204,
Illite [19]	412, 413, 416, 623, 633
Albite [25–27]	164, 167, 414, 415, 416, 505,506, 508, 553, 561, 565, 762,
Amorphous carbon [20,22,28]	1444, 1468, 1470, 1476, 1482
Black carbon [18,29]	1359,1569, 1608, 1614, 1616, 1618, 1628

Table 5

The characteristic infrared wavenumbers for the minerals possibly existed in the mentioned ceramic shards. The relevant sources have been reported within the brackets in the first column.

Minerals	IR wavenumbers (cm ⁻¹)
Hematite [31]	464, 467, 468, 469, 470, 473, 475, 476, 541, 542,
Quartz [31]	514, 521, 676, 691, 692, 693, 694, 695, 696, 698, 776, 777, 778, 780, 793, 794, 795,796, 1069, 1071, 1072, 1073, 1074, 1076, 1077, 1078, 1160, 1162
Calcite [32–33]	712, 716, 718, 830, 835, 876, 1428, 1433, 1436, 1437, 1439, 1441, 1457, 1459
Kaolinite [24,31–34]	542, 548, 920, 1038, 1043, 1041
Albite [31]	553, 561, 565, 575, 579, 581, 585, 645, 652, 657, 658, 719, 720, 723, 742, 744, 745, 752, 755,1047, 1097
Amorphous carbon [18]	1384, 1385, 1387

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References

- [1] G.M.A. Hanfmann, J.C. Waldbaum, *AJA* 72 (1968) 51–56.

- [2] H.G.M. Edwards, P. Colomban, B. Bowden, *J. Raman Spectrosc.* 35 (2004) 656–661.
- [3] D. De Waal, *J. Raman Spectrosc.* 35 (2004) 646–649.
- [4] C. Lofrumento, A. Zoppi, E.M. Castelluci, *J. Raman Spectrosc.* 35 (2004) 650–655.
- [5] H.G.M. Edwards, D.W. Farwell, C.P. Heran, H. Croft, A.R. David, *J. Raman Spectrosc.* 30 (1999) 139–146.
- [6] A. Brysbaert, P. Vandenaabeele, *J. Raman Spectrosc.* 35 (2004) 686–693.
- [7] R.J.H. Clark, L. Cridland, B.M. Kariuki, K.D.M. Harris, R. Witnall, *Chem. Soc. Dalton Trans.* (1995) 2577–2582.
- [8] D.C. Smith, M. Bouchard, M.J. Lorblanchet, *J. Raman Spectrosc.* 30 (1999) 347–354.
- [9] S. Shoval, P. Beck, *J. Therm. Anal. Cal.* 82 (2005) 609–616.
- [10] G. Velraj, K. Janaki, A.M. Musthafa, R. Palanivel, *Appl. Clay Sci.* 43 (2009) 303–307.
- [11] S. Shoval, *Opt. Mater.* 24 (2003) 117–122.
- [12] S. Shoval, O. Yofe, Y. Nathan, *J. Therm. Anal. Cal.* 71 (2003) 833–892.
- [13] J. Van deer Weerd, G.D. Smith, S. Firth, R.H.J. Clark, *J. Archaeol. Sci.* 31 (2004) 1429–1437.
- [14] D.A. Scott, S. Sheerer, D.J. Reeves, *Stud. Conserv.* 47 (2002) 184–194.
- [15] C.R. Ferring, T.K. Perttula, *J. Archaeol. Sci.* 20 (1983), 41–.
- [16] R. Goodall, J. Hall, R. Viel, P.M. Fredericks, *Archaeometry* 51 (2009) 95–109.
- [17] L. Burgio, R.J.H. Clark, *Spectrochim. Acta Part A* 57 (7) (2001) 1491–1571.
- [18] M.A. Legodi, D. De Waal, *Dyes Pigments* 74 (2007) 161–168.
- [19] S. Akyüz, T. Akyüz, S. Başaran, Ç. Bolcal, A. Güleç, *Vib. Spectrosc.* 48 (2008) 276–280.
- [20] S. Akyüz, T. Akyüz, S. Başaran, C. Bolcal, A. Güleç, *J. Mol. Struct.* 834–836 (2007) 150–153.
- [21] A. Raskovska, S.B. Minceva, O. Grupcea, P. Colomban, *J. Raman Spectrosc.* 41 (2009) 431–439.
- [22] J. Zuo, C. Xu, C. Wang, Z. Yushi, *J. Raman Spectrosc.* 30 (1999) 1053–1055.
- [23] K.H. Michaelian, *Can. J. Chem.* 64 (1986) 285–294.
- [24] R.L. Frost, P.M. Fredericks, J.R. Barlett, *Spectrochimica Acta Part A* 49 (1993) 667–674.
- [25] P. Matreski, G. Jovanovski, B. Kaitner, *J. Mol. Struct.* 924–926 (2009) 413–419.
- [26] S.E.J. Villar, H.G.M. Edwards, *Vib. Spectrosc.* 39 (2005) 88–94.
- [27] D.A. McKeown, *Am. Mineralogist* 90 (2005) 1506–1517.
- [28] J. Striova, C. Lofrumento, A. Zoppi, E.M. Castelluci, *J. Raman Spectrosc.* 37 (2005) 1139–1145.
- [29] J. Zuo, x. Zhao, R. Wu, G. Du, C. Xu, C. Wang, *J. Raman Spectrosc.* 34 (2003) 121–125.
- [30] M. Sendova, V. Zhelyascov, M. Scalera, M. Ramsey, *J. Raman Spectrosc.* 36 (2005) 829–833.
- [31] G.D. De Benedetto, R. Laviano, L. Sabbatini, P.G. Zamboni, *J. Cult. Herit.* 3 (2005) 609–616.
- [32] H.N. Rutt, J.H. Nicola, *J. Phys. C. Solid State Phys.* 7 (1974) 4522–4528.
- [33] A.-J. Xie, C.-Y. Zhang, y.-H. Shen, L.-G. Qui, P.-P. Xiao, Z.-Y. Hu, *Cryst. Res. Technol.* 41 (2006) 967–971.
- [34] D. Bilikiaris, S. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A.P. Moutsatsou, Y. Chrysosoulakis, *Spectrochim. Acta Part A* 56 (1999) 3–18.