

SPECTROSCOPIC AND X-RAY BASED MICROSTRUCTURAL INVESTIGATION OF THE EARLY-HARAPPAN POTSHERDS AND ESTIMATION OF FIRING TEMPERATURE FROM KUNAL ARCHAEOLOGICAL SITE, INDIA

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Abstract

In the present study, the archaeological potsherds excavated from Northern India's Early-Harappan Kunal site (3800 - 2200 BCE) were examined to understand the microstructural features of the potsherds and to estimate the firing temperature using Light microscopy, Mercury Intrusion Porosimetry (MIP), Scanning Electron Microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform Infrared spectroscopy (FTIR), and X-ray diffraction (XRD). For the characterization of ancient potsherds and understanding their strength and stability, mapping for chemical composition and estimation of firing temperature was carried out. Both low firing temperature and high firing temperature were estimated to ascertain the oxidizing and reducing conditions for firing based on mineralogical analysis and vibrational assignments. Fast quenching and ill firing were also noticed in one specimen. MIP showed porosity (n) of \approx 16% as well as a void ratio (e) of 0.19. The analysis indicated that the Harappan potters were very proficient in pottery-making skills.

Keywords: Firing temperature; Mercury intrusion porosimetry; Kunal; Early-Harappan; Pottery characterisation

Introduction

Archaeologists and conservators have long been interested in the studies of ancient potteries, the most commonly discovered artifacts during excavation, and investigating into the firing temperature of the potsherds to establish the relationship among production technique, mineralogical changes, and changes in the microstructure. There have been many discussions on open firing versus kiln firing [1]. It is reported that big and large Harappan pottery is mostly well fired. However, the kiss-marks, black blotches, and cramped pots indicate ill firing [1]. The redware though contains ferrous oxide that may have been fired under insufficient oxygen. Various studies and examinations have been conducted to estimate the firing temperature and environmental conditions of the firing of black-and-red ware.

The introduction of heat for the production of pottery was experimented with by Roman potters and glassmakers dating back to around 3000 B.C. Chinese potters from the 2nd to 7th century (Han dynasty to Sui and Tang dynasty) developed methodologies of firing the ceramics to a very high temperature, even some ceramics like Yue ware were fired above 1300°C. The

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production of alumina-rich porcelain with hard-paste was possible due to the availability of kaolin was helpful in developing the fritware technology [2]. In the reducing atmosphere, it was also reported that a liquid phase develops at 700°C between the ferrous oxide and clays that facilitate better sintering [2]. That is why Mesopotamians were able to get the perfect firing at low temperatures due to micro-sized silts. Once the liquid phase is achieved at the interface, the better soldering of the grains takes place which resulted in reducing the porosity, and in porcelain, the maximum volume of the clay body reaches to liquid state which helps them in rendering the optical transparency to the pottery [2]. Mesopotamian ceramics were fired at temperatures 850-900°C, sufficient for the perfectly built ceramics [3, 4]. The inclusions, plastic or non-plastic, also contribute to pore size distribution because, during the thermal expansion, non-plastic inclusions leave voids at the grain boundaries which upon cooling also induces cracks in the ceramic structure [5, 6]. On firing, the clay minerals undergo various stages of reactions such as dehydration by losing physically and chemically bonded water molecules, and transformation of α -quartz into β -quartz during quartz inversion followed by sintering. The precise determination of the firing temperature becomes much more complicated due to variation in the clay composition [3]. Two methods of firing pottery have been practiced from archaeological times: the kilns and open pits [4]. The temperature reaches the same level in both methods of firing but the kiln can retain the temperature with better efficiency about 100°C more to open pits.

The study of characterization of the pottery, its microstructure, the degree of vitrification, inclusions, and slips have been conducted by using powder x-ray diffraction studies, optical microscopy, SEM-EDX, secondary electron, and backscattered electron, EDX analysis [4, 8-11]. PIXE was also employed for the determination of the elemental composition of the painted surfaces on the terracotta pots [12]. The introduction of these scientific technologies reduces the requirement of sample size significant Laser-Induced Breakdown Spectroscopy (LIBS) also helped in micro-sampling [2]. Estimation of firing temperature is based on mineralogical changes and colour changes during firing, hardness, sintering, vitrification, and porosity that can be studied with thermogravimetric analysis (TGA), thermal expansion and differential thermal analysis (DTA), Mossbauer spectroscopy, Fourier transform infrared spectroscopy (FTIR), etc. [4, 9-11, 13, 14]. Mercury Intrusion Porosimetry (MIP) has been used as a potential tool for the study of porosity and pore size distribution. Nitrogen adsorption and water adsorption have also been used as other techniques for the porosity measurement of potteries. But the limitation of nitrogen adsorption and water adsorption methods is that only pore volume can be measured with water adsorption and pore size distribution cannot be determined whereas, nitrogen adsorption can only measure the micro to mesopores and not the macropores [15].

The purpose of the present study is to identify the chemical composition of the potsherd, propose an estimated firing temperature, and measure porosity and pore size distribution. In this research, spectroscopic techniques (FTIR, XRD) and microscopic techniques (digital microscopy and SEM-EDX) have been used for the investigation of the samples. Fourier Transform Infrared (FT-IR) and X-ray diffraction (XRD) were used for the mineralogical composition. A combined study by FTIR, XRD, and SEM-EDX was done to estimate the firing temperature of the pottery samples. MIP has been applied to estimate the porosity and pore size distribution which will substantiate the results obtained from the other techniques. This research work focuses on two main areas: the mineralogical composition and the firing condition and firing temperature [16-21].

Kunal archaeological site

Kunal is a village in tehsil Ratia of district Fatehabad (earlier in Hissar) in the state of Haryana, India. The graphical location of the site is 29°30'N lat. and 75°41'E long. It belongs to Hissar Division and the core area of the settlement is three to four acres with the total area expanding to nine acres (Fig. 1a). Excavations at this site provided various unique items that are

extremely significant to understanding the Early-Harappan culture, which also enriches our knowledge of the early Indian culture [5]. The archaeological excavations at Kunal were started by J.S. Khatri and M. Acharya in 1986 and further excavations are still continuing with a few field-season gaps. Artifacts excavated include bone tools, copper arrowheads, fish hooks, and micro-blades of chalcedony. The Harappan pottery has four categories: redware, buffware, grey ware, and black-and-red ware [1]. The paintings evidenced in black on the red surface, chocolate or purple-black on the buff surface, and white or creamy on the black surface of the black-and-red ware. The Harappan potters used the clay of fairly good quality and generally well levigated as revealed by the cohesion of the clay particles. The tempering materials such as lime, mica, or sand have been mixed proportionately in the clay [1]. Kunal has yielded all the varieties of pottery (six pottery fabrics of Early-Harappan) which were earlier reported from the excavation site of Kalibangan. The late age potteries of Kunal are bichrome and redware painted in two colors mostly with a black outline filled with white [6]. The pottery collection is mainly dominated by the Hakraware. Other than wheel-made pottery, some hand-made pottery was also found. Of all the potteries, the most significant is the dull red (or red washed) pottery with wavy incised decorations in two colors: black outline and white filling. Some more designs are faunal and floral motifs, crisscross diamond-shaped geometric patterns [5]. Extremely important are a few potsherds of jars with a clear impression of fine and rough cloths on the inner surface [5].



Fig. 1. (a) Location of Early-Harappan Kunal site in Haryana, India (b) Excavated trench with buried pottery pieces visible (circled).

Materials and Methods

The pottery samples investigated were recovered during the archaeological excavation from Kunal. The samples were collected from 50-60cm depth of the soil surface (Fig. 1b). All the samples selected for this study were red pottery pieces. The samples were labelled as KPS 1, 2, 3, 4 and 5 (5.1 and 5.2) (Fig. 2). Only in the sample KPS 5, both sides of the sample were red, but the inner part was black in colour which indicated that the sample is ill-fired. After the removal of superficial depositions (dust and sand particles) by using ethanol, the potsherds were finely ground into powder in a mortar and pestle and the powdered samples were subjected to analysis. All samples were pre-heated at 150-200°C for two hours to remove extra moisture trapped within the potsherds before any analysis. For XRD and FTIR measurements powdered samples were preliminarily

examined at 50X magnification using a Dinolite digital microscope with an adjustable polarizer for the clarity of the microscopic images.



Fig. 2. Selected pottery samples for the microstructural study.

Instrumentation

FT-IR spectroscopy was used for the chemical composition and mineralogical properties of clay minerals and also for the estimation of the firing temperature of the potsherds. Mid-FTIR spectra of the samples in the wavenumber range from 4000 to 400cm⁻¹ were obtained at 4cm⁻¹ resolution recorded on a Perkin Elmer spectrometer (FT-IR spectrum 2) using the KBr pellet.

For the phase determination of the powdered pottery samples, Powder X-ray diffraction was conducted on the Panalytical X-Pert Pro Advance diffractometer with Xe-methane proportional detector, employing CuK α (λ = 0.15408nm) radiation generated at 40kV and 30mA with a scan rate of 0.01s⁻¹. Powdered samples were placed on the sample holder evenly dispersed and were introduced in the X-ray diffractometer. To identify the crystalline phases in the clay minerals, the X-ray diffractograms were obtained in the 2 θ range of 10–80°C at room temperature. Following the standard procedures of interpretation of XRD, the mineralogical composition was ascertained [8].

All samples were investigated microscopically using the backscattered electron (BSE) mode on a Nova Nano field emission scanning electron microscope (FE-SEM 450 (FEI)) at low vacuum (between 150 to 200Pa), coupled with an energy-dispersive X-Ray (EDX) spectroscopy, using JEOL 5500 LV equipment at an accelerating voltage of 20kV. EDX analysis was done to obtain the percentage concentration of the elemental composition of all samples. None of the samples were coated for the SEM examination and were placed directly onto the sample holder.

The precise distribution of the pores in the pottery samples was determined using mercury intrusion porosimetry employing pore master 60 (Quantachrome Instrument, USA). The sample was characterized to understand the pore distribution and pore structure of different sizes in the specimen. The instrument pressurizes the mercury (from 0 to 60000psi) into the sample and measures the corresponding volume of mercury intruded to give the pore size (ranging from a few nanometers to several hundred micrometers). The specific gravity (G) of the sample was determined using an ultra-pycnometer (ULTRAPYC-1200e, Quantachrome

Instruments, USA) in which inert gas helium was used to calculate the volume of the sample to determine the specific gravity G. A known weight the of the oven-dried sample was taken and the testing method suggested in the code ASTMD 5550, 2014 [9] was followed.

Results

All the data obtained from digital microscopy, FTIR measurements, XRD measurements, SEM viewing, elemental scanning and EDX analysis, the comparison of results and their interpretations have been discussed below.

Light microscopy

When the samples were examined under the digital microscope at 50X (Fig. 3), in sample KPS 1, the black carbon was deposited on the surface of the potsherd which was clearly visible in terms of black accretions and black lines. In addition to the presence of carbon, the black deposition might also be due to the presence of a small amount of manganese. The microscopic image suggested that the pot might have been used for cooking purposes. In sample KPS 2, a white precipitate was observed deposited on the surface of the potsherd which indicated the presence of secondary calcite that is generally found in porous potsherds in burial conditions. In sample KPS 3, faded black paint patches can be seen on the potsherd and had surface erosion. White tiny particles of mica have also been noticed in this sample. In sample KPS 4, white deposits were also seen as in KPS 2. Some blister-like appearance was observed on the surface of the sample KPS 4. In sample KPS 5, curvy lines were seen which showed that the manufacturing technique must be wheel turned.



Fig. 3. Microscopic photographs of the sample surfaces taken at 50X magnification

FTIR analysis

The FTIR spectra of the samples are shown in figure 4 and the identification of clay minerals was accomplished with the help of various reference spectra [10]. The spectra showed the absorption bands in the functional group region around 3432 - 3451 cm⁻¹ and 1623 - 1632 cm⁻¹ were the characteristic bands of absorbed water molecules. The absorption bands in a range of 2850 - 2960 cm⁻¹ which is due to the C-H stretching of organic carbon that indicated the presence of organic contaminants. In all samples, weak bands at 2923 - 2928 cm⁻¹ (Table 1), due to C-H stretching also indicate the appearance of organic carbon [22-25].

Samples	O-H group from adsorption of water	C-H stretching of CH3 group from organic carbon	CH2 symmetrical stretching	C=O stretching of calcite	H–O–H bending of residual water	C-O stretching of calcite	C-H bending of organic carbon	Si-O-Si stretching of silicates	Al-O-Si stretching of aluminosilica tes	Si-O stretching of clay minerals	C-O stretching of calcite	Si–O stretching of quartz	Si-O bending of quartz	Fe-O bending of magnetite	Si-O-Si bending of silicates
KPS-1	3451.89	2926.39	-	-	1632.6	-	1383.66	-	1067.98	-	-	778.34	-	-	472.08
KPS 2	3447.84	2923.93	2859.3		1631.55		1383.83	100	1074.73	1770	-	788.54		577.26	463.78
KPS 3	3444.94	2924.53	-	-	1630.54	-		-	1073.18	-	-	779.70	693.85	570.88	462.36
KPS 4	3437.73	2927.2	2851.3	-	1633.18		1384.34	-	1085.2	1045.65	-	786.47		565.82	476.04
KPS 5.1	3434.47	2924.48	2863.3	-	1630.54	-	1384.28	-	1065	-	-	785.77	693.27		464.98
KPS 5.2	3432.12	2928.07 2963.2	2859.3	1795.97 2515.43	1623.63	1449.99	-	1125.26	20	-	874.64	-	712.58	1	-

Table 1. FTIR absorption bands with respective vibrational assignments

The band assignments in the functional group and fingerprint regions prominently indicated the presence of quartz and feldspar as dominant minerals (Si-O, Al-O-Si, Si-O-Si), organic contribution (C-H stretching and C-H bending), weak calcite bands (C-O), and magnetite (Fe-O bending) [11].



Fig. 4. FT-IR spectra of all potsherd samples collected from Kunal site.

Mineral phases as observed by XRD diffractograms

The mineral phases of the pottery samples obtained from the diffractograms are presented in Table 2 and the diffraction patterns are shown in figure 5. Crystalline phases of the minerals were identified using data from the Joint Committee of Powder Diffraction Standards [26, 27]. The results in table 2 shows that quartz and microcline (high-temperature silica) are prominent constituents in all samples, magnetite was also found in all samples, but hematite was not seen in any of the samples. Other minerals such as calcite, orthoclase, albite, illite, muscovite, biotite, lepidolite, anorthite, and mullite (high-temperature silica) were also detected. The general constituents of the raw materials of potsherds such as maghemite, goethite, and dickite were completely absent in all the samples since goethite and dickite generally decompose at low temperatures [28].



 Table 2: Mineral phases detected by the X-ray diffractogram (Corrected)



Fig. 5. XRD diffractogram of the potsherd with mineral phases (q = quartz; c = calcite; M = muscovite; m = magnetite; m1 = microcline; o = orthoclase; b = biotite; $\mu = mullite$; a = albite; A = anorthite; L = lepidolite; d = dolomite).

Specific gravity, porosity, and pore size distribution

Each sample was analyzed for specific gravity in triplicates and the average value of G, calculated is presented in Table 3.

sumple and 5.2 represents not completely med sumple.)							
Sample ID	KPS 4	KPS 5.2					
E	0.10	0.10					
n (%)	9.38	8.94					
Specific gravity (G)	2.74	2.62					

 Table 3. The voids ratio (e), porosity (n), and the specific gravity (G) of the samples (KPS represent completely fired sample and 5.2 represents not completely fired sample.)

The pore size distribution was obtained by the intrusion of the total volume of mercury (V_m) at a given pressure. The mercury is used because of its non-wetting nature with larger contact angle ($\theta = 140^\circ$) and surface tension ($\sigma = 0.48$ N/m) values. Its intrusion into the pores would be possible only by the application of external pressure which can be obtained by equation 1 [12]. However, this equation takes the cylindrical geometry of the pores into account which is a big drawback of the technique [15].

$$P = \frac{4\sigma\cos\theta}{d} \tag{1}$$

Here, P is the pressure applied, and d is the corresponding diameter of the pore which gets filled with the mercury, θ being the contact angle, and σ being the surface tension. The pore distribution-related parameters were acquired using the standard ASTM D4404-84 guidelines [13] and Table 3 shows the final voids ratio of sample KPS 4 and KPS 5.2. As per the categorization of the porous matrix [29-31], the samples comprised of a larger proportion of the macropores with major pore diameter were in 0.01 - 1µm the range (Fig. 6a). Moreover, all the samples exhibited a monomodal pore size distribution.

The cumulative pore volume of both samples showed similar types of curves showing broad contributions. Both potsherds presented higher total pore volumes and higher pore size. The prominent pore size diameter to pore volume was found between $0.3 - 3\mu m$ and around $2/3^{rd}$ of the entire volume distributions. The preferential size of pores i.e., mean pore diameter was found to be in the range of around $0.2 - 0.3\mu m$ and $1-2\mu m$ for the samples KPS 5 and KPS 4 respectively as can be noticed in figure 6b. The MIP technique applied for these pottery samples demonstrated a higher proportion of uniform pore size.



Fig. 6 (a) Cumulative volume of mercury intruded vs pore diameter as obtained from the mercury intrusion porosimeter. (b) Differential pore size distribution

Discussion

FTIR is one of the preferential methods of evaluating the firing temperature, especially for low fired ceramics. The firing temperature provided information on the firing technology and the quality of the pottery. These ceramics were fired below the thermal crystallization of firing silicates, and their meta-clay composition was amorphous as detected by the XRD method [32]. The FTIR profile of the samples (Table 1) shows that in the functional group region all samples contained hydroxyl group arising due to weak absorption of water at 3432 -3451cm⁻¹ but did not reflect any inner hydroxyl bands between 3600 - 3700cm⁻¹ which is suggestive of the temperature of kiln firing higher than 500°C [33]. The water absorption bands observed around 1630cm⁻¹ due to H-O-H bending vibration was probably due to the absorption of water molecules during burial condition as the pottery pieces were recovered from the excavation. The absorption bands at 2924 - 2963cm⁻¹ due to C-H stretching of CH₃ group and 1383cm⁻¹ due to C-H bending organic carbon indicates the presence of organic contaminants and also hint that firing temperature might be lower than 1000°C as above this temperature organic contaminant would burn out. Another way to estimate the firing temperature of the kiln is to check the presence of two peaks at 915 and 875cm⁻¹ which occur due to Al-O-H and absence of band at 915cm⁻¹ suggests the firing temperature above 500°C and the absence of band at 875cm⁻¹ hints at firing temperature above 750°C as both bands disappear above the temperature 500°C and 750°C respectively [14]. The band at 915cm⁻¹ was not found in any of the samples and also the band at 875cm⁻¹ was found only in KPS 5.2, thereby indicating the

firing temperature of all the samples was above 750°C except KPS 5.2 which was fired at an insufficient temperature [15]. The 875cm⁻¹ band observed in KPS 5.2 arising due to C-O stretching vibration of calcite provides evidence of the insufficient firing temperature in that portion of the pottery as the decomposition temperature of calcite is between 750-900°C [34-39]. Generally, above 850°C, calcite decomposes and transforms into high-temperature minerals such as calcosilicates, alumina-calcosilicates, wollastonite, gehlenite, plagioclase feldspars like anorthite, pyroxenes like diopside [40]. The data shows that sample KPS 5.2 might have been ill-fired and reflects an exception from the remaining samples (KPS 2, KPS 3 and KPS 4 and KPS 5.1) in which no calcite is found.

Quartz being the prominent mineral in the pottery is also observed in FTIR spectra of all samples. The characteristic absorption vibration bands of quartz appeared 1065 - 1085cm⁻¹ due to Al-O-Si symmetrical stretching and 775 - 785cm⁻¹ due to Si-O symmetrical stretching, at 693cm⁻¹ due to Si-O symmetrical bending and at 464cm⁻¹ due to Si-O asymmetrical bending. The presence and absence of the band at 693cm⁻¹ reflected the crystalline and amorphous form of the quartz respectively. In the sample KPS 3 and KPS 5.1, the 693cm⁻¹ peak has appeared thus indicating the crystalline state of quartz mineral. The samples KPS 3 and KPS 5.1 also indicate quartz of thin particle size and also the weak Al–O–Si stretching absorption peaks of feldspar at 693cm⁻¹ in these two samples [17]. This peak also refers to the presence of feldspar in these two samples [17]. Another band assignment that helps in ascertaining the firing temperature is at 1065 - 1085cm⁻¹ arising due to Al-O-Si stretching of aluminosilicates that has been detected in all samples except KPS 5.2. This band assignment indicates the firing temperature of the samples in the range of $800 - 900^{\circ}$ C [18]. Interestingly, in the FTIR spectra of KPS 4, there are two peaks at 1045 and 1085cm⁻¹ (Table 1) which appeared probably due to the splitting of the band generally found at 1042 cm^{-1} at 700° C. The band at 1042 cm^{-1} splits into bands at 1045 and 1085cm⁻¹ when the temperature is elevated over 800° C [16, 18].

Quartz and feldspar were noticed in all samples in the XRD diffractograms which indicated that the kiln firing temperature was around or more than 800°C since these two minerals are stable at a wide range of temperature and do not undergo any transformation up to 1000°C [19]. Quartz was present as the main composition of the clay, however, some quartz might have also been added as a fluxing material [41, 42]. The presence of calcite phase was also noticed in two samples KPS 1 and KPS 5.2 though in traces only which indicated the non-calcareous type of clay as at temperature 600-850°C calcite tends to break down into CaO and CO_2 at approximately 600–850°C and forms calcium silicates in diopside-wollastonite-silica system at 850–900°C [43-45]. The absence of calcium silicate further corroborated the non-calcareous type of clay which was also supported by SEM-EDX analysis. The high-temperature mineral phase microcline and alkali feldspar were observed in all the samples [20]. The samples KPS 1, KPS 2, KPS 3, KPS 5.1, and KPS 5.2 also contained minerals that occur at low firing temperature, such as muscovite, illite, dolomite, biotite. The presence of silica and feldspar indicated the firing temperature 800°C or above but the presence of illite and muscovite indicated the firing temperature lower than 1000°C as illite disappears over 1000°C [21].

The alkali feldspar group mineral orthoclase was noticed in KPS 5.1 sample [46-48]. The plagioclase feldspar group mineral albite was quite abundant in some of the samples (Table 2). Due to the identical structure of the feldspar group minerals, they exhibit similar properties and tendencies [48].

The atmospheric condition of firing can be ascertained by the presence and concentration of hematite and magnetite as reducing atmospheric condition indicates higher concentration of magnetite and oxidizing condition indicates higher concentration of hematite. I/I_0 which is the ratio of amount of iron oxides (Fe₃O₄ / Fe₂O₃) can predict the atmospheric condition in which the potsherds were fired. ($I/I_0 > 1$) indicates higher concentration of magnetite and ($I/I_0 < 1$) indicates higher concentration of hematite [23]. Since we found only the peaks corresponding to magnetite, so samples with a higher amount of magnetite showed that they were fired in a

closed kiln and the magnetite phase also reflected the firing temperature above 800°C which was present in KPS 2, KPS 3 & KPS 4 [49]. The presence of magnetite was also supported by IR absorption bands at 464cm⁻¹ which was due to Si–O–Si bending of silicates and bands present between 565 - 578cm⁻¹ in samples KPS 2, KPS 3, KPS 4 were characteristic bands of magnetite arising due to Fe–O bending. XRD and FTIR both showed complementarity of the mineral identification results.

These results implied that samples were fired above 800°C but below 1000°C and the craftsmen of Kunal were well versed in firing the potteries in both oxidizing and reducing environmental conditions. Depending upon the different weather conditions and fluctuations in wind movement and velocity, the firing temperature may drift swiftly from reducing to oxidizing atmospheric conditions. However, complete oxidation of ancient pottery pieces has been rare because the organic materials present in the clay do not get sufficient firing time for complete combustion to escape from pottery [11]. Since the colour of the pottery is temperature dependent, the incomplete combustion of the organic materials lead to variation in the colour of the pottery. As the firing kiln temperature increases, the colour of the pottery changes from orange to light red hue at 700-800°C to dark red hue at 900°C [50-59]. As progress in pottery making is related with firing temperature (the higher the firing temperature, the more advanced the technique), it is evident that the skills of ancient Harappan potters were well developed and fairly advanced at that time [24]. Scanning electron microscopy has also long been used to characterize the morphology, degree of vitrification of archaeological ceramics which actually helps in estimation of the firing temperature of the pottery [53, 54]. The elemental weight percentage in the samples was calculated via Energy dispersive X-ray spectroscopy and the uniform distribution of elements in the whole volume was measured through elemental mapping (Figs. 7 and 8).



Fig. 7. Elemental mapping of KPS 4 sample. O-KA, C-KA, Si-KA, Al-K, Fe-KA, Cl-KA, K-KA, Ca-KA; Image size: 1024 x 768, Mag: 2400x, HV: 30.0kV

The elemental mapping of both the samples KPS 4 and KPS 5.2 show that Si, Al and K are distributed throughout the area in both the cases. The presence of carbon in the sample KPS

5.2 is more distributed in the matrix whereas in KPS 4, the carbon has a few areas of concentration where there is a depletion of silicon. Iron and chlorine are also seen more distributed in KPS 5.2 in comparison with KPS 4 where these elements are seen in the smaller area of concentrations.



Fig. 8: Elemental mapping of KPS 5.2 samples. O-KA, C-KA, Si-KA, Al-K, Fe-KA, Cl-KA, K-KA, Ca-KA; Image size: 1024 x 768, Mag: 2400x, HV: 30.0kV

Major and minor elements detected in the EDX analyses has been presented in Table 4.

Elements	Series	KPS 4	KPS 5.2
0	K-Series	48.83	49.25
Si	K-Series	21.05	18.46
С	K-Series	16.09	18.18
Al	K-Series	7.10	6.35
Fe	K-Series	3.00	4.20
К	K-Series	2.74	2.58
Ca	K-Series	1.00	0.61
Cl	K-Series	0.19	0.37
Total		100.00	100.00

Table 4. Elemental concentration (normalised wt %) of the archaeological potteries of Kunal site.

The same type of clay might have been used from the origin for making potteries which is further corroborated by the similar elemental concentrations detected by SEM-EDX analysis. The elemental concentrations in Table 4 indicate silica, alumina, organic carbon, and iron oxide as major components whereas the minor presence of K, Ca and Cl, indicated elements of flux materials. As indicated in the Table 3, the percentage concentration of potassium in KPS 4 (2.73%) is greater than its concentration in KPS 5.2 (2.58%) indicating the higher firing temperature for KPS 4 than KPS 5.2 which also supports the dark colour of pottery part in KPS 5.2 due to insufficient firing. The presence of potassium as flux as mentioned above actually

helps in lowering the firing temperature, initiating the sintering process, and also in vitrification, however, exact estimation of the firing temperature is difficult using only the mineralogical data [55]. The other fluxing element calcium was much less in concentration in all samples (1% or lower) which further proved the non-calcareous type of the clay as for the calcareous clay the amount of calcium has to be above 6% [56]. The SEM images in figure 9a and 9b shows some regions of smooth surfaces which suggest the vitrification stages in the pottery samples. In figure 9a, the vitrified area is more prominent than in figure 9b which suggests the KPS 4 attained higher firing temperature in oxidizing condition around 800°C whereas KPS 5.2 was fired in reducing condition at slightly lower temperature [33, 53]. It has been observed that clay composition and the kiln firing conditions influence the production of different minerals [56], like hematite is produced upon pottery fired in oxidizing atmosphere [26]. Quartz being primary mineral in the potteries does not undergo any transformation even at a range of temperatures, however, some secondary minerals are produced due to the development of metastable phases of minerals during firing [56 - 58].



Fig. 9: SEM images and EDX spectra of (**a**) sample KPS 4 (**b**) sample KPS 5.2. Initial stage of vitrification is clearly noticed in KPS 4 by isolated smooth area.

Conclusion

Characterization of the selected clay potsherds from Kunal, the archaeological site of Haryana, with the help of MIP, FT-IR, XRD and SEM-EDX methods were helpful in providing an insight into past cultures. There is an exceptional behaviour observed in one potsherd whose exposed surface was red in color but the middle portion was black which showed the firing temperature did not reach the optimum level in the inner part of the pottery and the pottery was subjected to cooling. The reason for this significant color change was the fast quenching without allowing the pottery to reach sufficient temperature for its adequate firing. The results obtained from SEM also showed dramatic changes in the sample's microstructure. Various band assignments in the FTIR spectra showed the firing temperature of all samples above 800 °C but below 1000°C except the sample KPS 5.2 which was subjected to insufficient firing at 750°C or a little lower. This result was in agreement with XRD mineralogical analysis further corroborated by SEM-EDX analysis. Interpretation of all those analyses indicated both low

firing (less than 800°C) and high firing (more than 800°C) and indicated the oxidizing and reducing firing conditions [59]. The potsherds examined under light microscopy revealed the pottery making techniques. It indicated that the potteries were made via both handmade and wheel turned techniques. Handmade potsherds have rough surfaces without any lines on it. While wheel turned potsherds have comb-like curvy line patterns.

This research based on the complementarity of analytical instrumentations such as MIP, SEM-EDX, XRD and FTIR, etc. were very useful in determining the mineral phases and composition, firing temperature, methods of firing, conditions of firing atmosphere, manufacturing techniques, etc. of the potteries. This paper also developed first-hand information on pyrotechnology and other mineralogical aspects of ceramics from the very important site of the pre-Harappan period.

Acknowledgement

Authors would like to thank Vice Chancellor, National Museum Institute and Dr. Banani Bhattacharya, Haryana State Archaeology for making the sample available for this research. The authors are thankful to Prof. D. N. Singh, IIT Mumbai for MIP analysis. The help extended by Shri Udesh Kumar is gratefully acknowledged.

References

- [1] K.L. Rasmussen, A. Guillermo, A.D. Bond, K.K. Mathiesen, S.D. Vera, *Pottery firing temperatures: a new method for determining the firing temperature of ceramics and burnt clay*, Journal of Archaeological Science, 39, 2012, pp. 1705–1716.
- [2] D.K. Chakrabarti, Size of the Harappan settlements, Essays in Indian Protohistory, 1979, pp. 205–215.
- [3] P. Colomban, *The Destructive/Non-Destructive Identification of Enameled Pottery, Glass Artifacts and Associated Pigments—A Brief Overview,* Arts, 2, 2013, pp. 77–110, https://doi.org/10.3390/arts2030077.
- [4] Y. Maniatis, *The Emergence of Ceramic Technology and its Evolution as Revealed with the use of Scientific Techniques*, From Mine to Microscope: Advances in the Study of Ancient Technology, Oxbow Books, Oxford, 2009, p. 1–18.
- [5] A. Hein, V. Kilikoglou, Modeling of the microstructure of ancient functional ceramics and assessment of their performance, Procedia Structural Integrity, 1st International Conference of the Greek Society of Experimental Mechanics of Materials, 10, 2018, pp. 219–226, https://doi.org/10.1016/j.prostr.2018.09.031.
- [6] A. Hein, N.S. Müller, P.M. Day, V. Kilikoglou, *Thermal conductivity of archaeological ceramics : The effect of inclusions , porosity and firing temperature*, Thermochimica Acta, 480, 2008, pp. 35–42, https://doi.org/10.1016/j.tca.2008.09.012.
- [7] N.I. Zagorodny, C. Volzone, M. Morosi, B. Balesta, A Systematic Evaluation of the Firing Temperatures of Archaeological Pottery from Catamarca, Argentina, National University of La Plata Faculty of Natural Sciences and Museum, 2016, pp. 1-12, https://core.ac.uk/download/pdf/141500123.pdf
- [8] M.P. Mata, D.R. Peacor, *Transmission Electron Microscopy (TEM) Applied to Ancient Pottery*, Archaeometry, 2, 2002, pp. 155–176.
- [9] Y. Maniatis, M.S. Tite, *Technological examination of Neolithic-Bronze Age pottery from central and southeast Europe and from the Near East*, Journal of Archaeological Science, 8, 1981, pp. 59–76.
- [10] M.S. Tite, Y. Maniatis, Examination of ancient pottery using the scanning electron microscope, Nature, 257, 1975, pp. 122.
- [11] Y. Maniatis, M.S. Tite, Examination of Roman and medieval pottery using the scanning

electron microscope, Acta Praehistorica et Archaeologica, 9, 1978, pp. 125-130.

- [12] F.P. Romano, L. Pappalardo, N. Masini, G. Pappalardo, F. Rizzo, *The compositional and mineralogical analysis of fired pigments in Nasca pottery from Cahuachi (Peru) by the combined use of the portable PIXE-alpha and portable XRD techniques*, Microchemical Journal, 99, 2011, pp. 449–453.
- [13] Y. Maniatis, A Scanning Electron Microscope Examination of the Bloating of Fired Clays, Transactions And Journal of the Britain Ceramic Society, 74(7), 1975, pp. 229-232.
- [14] Y. Maniatis, V. Perdikatsis, K. Kotsakis, Assessment of in-site variability of pottery from Sesklo, Archaeometry, 30(2), 1988, pp. 264-274, https://doi.org/10.1111/j.1475-4754.1988.tb00452.x
- [15] C. Volzone, N. Zagorodny, Mercury intrusion porosimetry (MIP) study of archaeological pottery from Hualfin Valley, Catamarca, Argentina, Applied Clay Science, 91–92, 2014, pp. 12–15, https://doi.org/10.1016/j.clay.2014.02.002.
- [16] M. Acharya, Kunal Excavations (New Light on the Origin of Harappan Civilization), Department of Archaeology & Museums, Haryana, 2008.
- [17] B.B. Lal, Excavations at Kalibangan, the early Harappans, 1960-1969, Archaeological Survey of India, Haryana, 2003.
- [18] T. Broekmans, A. Adriaens, E. Pantos, Analytical investigations of cooking pottery from Tell Beydar (NE-Syria), Nuclear Instruments and Methods in Physics Research B, Beam Interactions with Materials & Atoms, 226, 2004, pp. 92–97.
- [19] M.H. Hey, International Mineralogical Association: commission on new minerals and mineral names, Mineralogy Magazine, 46, 1982, pp. 513–514.
- [20] * * *, A. D5550, Standard test method for specific gravity of soil solids by gas pycnometer, Annual Book of ASTM Standards, West Conshohocken, 2014.
- [21] V.C. Farmer, Infrared spectroscopy in clay mineral studies, Clay Mineralogy, 7, 1968, pp. 373–387.
- [22] G.R. Annamalai, R. Ravisankar, A. Naseerutheen, A. Chandrasekaran, K. Rajan, Application of various spectroscopic techniques to characterize the archaeological pottery excavated from Manaveli, Puducherry, India, Optik - International Journal of Light Electron Optics, 125, 2014, pp. 6375–6378.
- [23] D. Seetha, G. Velraj, Spectroscopic and statistical approach of archaeological artifacts recently excavated from Tamilnadu, South India, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 149, 2015, pp. 59–68.
- [24] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, **Handbook of mineralogy**, Mineral Data Publication, Tucson, 1990.
- [25] A.M. Saviuc-Paval, I. Sandu, I.M. Popa, I.G. Sandu, V. Vasilache, A.V. Sandu, Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements I. Synthesis and SEM-EDX and mu-FTIR Analysis, Revista de Chimie, 63(1), 2012, pp. 40-48.
- [26] * * *, Mineral Powder Diffraction File: Search Manual, J.I.C. for D. Data, A.C. Society, The Centre, 1986.
- [27] L.G. Berry, Powder diffraction file joint committee on powder diffraction standards, 1973, Ni File, 4, 1973, p. 850.
- [28] M. Maggetti, C. Neururer, D. Ramseyer, *Temperature evolution inside a pot during experimental surface (bonfire) firing*, Applied Clay Science, 53, 2011, pp. 500–508. https://doi.org/10.1016/j.clay.2010.09.013.
- [29] E.W. Washburn, The dynamics of capillary flow, Physics Review, 17, 1921, pp. 273.
- [30] * * *, ASTM D4404-84, Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry, ASTM International, 2010, https://doi.org/10.1520/D4404-10.tion.
- [31] H.Y. Moon, H.S. Kim, D.S. Choi, *Relationship between average pore diameter and chloride diffusivity in various concretes*, Construction and Building Materials, 20, 2006,

pp.725–732.

- [32] S. Shoval, *The firing temperature of a Persian-period pottery kiln at Tel Michal, Israel, estimated from the composition of its pottery*, Journal of Thermal Analysis and Calorimetry, 42, 1994, pp. 175–185.
- [33] G. Velraj, K. Janaki, A.M. Musthafa, R. Palanivel, Spectroscopic and porosimetry studies to estimate the firing temperature of some archaeological pottery shreds from India, Applied Clay Science, 43, 2009, pp. 303–307.
- [34] R. Ravisankar, S. Kiruba, C. Shamira, A. Naseerutheen, P.D. Balaji, M. Seran, Spectroscopic techniques applied to the characterization of recently excavated ancient potteries from Thiruverkadu Tamilnadu, India, Microchemical Journal, 99, 2011, pp. 370–375.
- [35] S.N. Ghosh, Infra-red spectra of some selected minerals, rocks and products, Journal of Material Science, 13, 1978, pp. 1877–1886.
- [36] F. Elsass, D. Olivier, Infra red and electron spin resonance studies of clays representative of the sedimentary evolution of the basin of Autun, Clay Mineralogy, 13, 1978, pp. 299– 308.
- [37] S. Shoval, *Oxford Handbooks Online Fourier Transform Infrared Spectroscopy (FT-IR)*, edited by Alice Hunt, **UCL Institute of Archaeology**, 2017, pp. 1–22.
- [38] L. Damjanović, I. Holclajtner-Antunović, U.B. Mioč, V. Bikić, D. Milovanović, I.R. Evans, Archaeometric study of medieval pottery excavated at Stari (Old) Ras, Serbia, Journal of Archaeological Science, 38, 2011, pp. 818–828.
- [39] S. Akyuz, T. Akyuz, S. Basaran, C. Bolcal, A. Gulec, FT-IR and micro-Raman spectroscopic study of decorated potteries from VI and VII century BC, excavated in ancient Ainos – Turkey, Journal of Molecular Structure, 836, 2007, pp. 150–153. https://doi.org/10.1016/j.molstruc.2006.12.011.
- [40] R.P. Silva, D.R.G. Tudela, Firing temperature determination and thermoluminescence dating of a brick with uneiform characters found in the ruins of Anceint Babylon, Revista Do Museu De Arqueologia Etnologia, 28, 2017, pp. 58–69.
- [41] K. Kihara, An X-ray study of the temperature dependence of the quartz structure, European Journal of Mineralogy, 2(1), 1990, pp. 63–77.
- [42] R. Ravisankar, S. Kiruba, A. Chandrasekaran, G. Senthilkumar, C. Maheswaran, Analysis of ancient potteries of Tamilnadu, India by spectroscopic techniques, Indian Journal of Science and Technology, 3, 2010, pp. 858–862.
- [43] M. Maggetti, *Phase analysis and its significance for technology and origin*, Archaeological Ceramics, 1982, p. 121–133.
- [44] T. Peters, R. Iberg, *Mineralogical changes during firing of calcium-rich brick clays*, Ceramic Bulletin, 57, 1978, pp. 503–509.
- [45] M.J. Trindade, M.I. Dias, J. Coroado, F. Rocha, Mineralogical transformations of calcareous rich clays with firing : A comparative study between calcite and dolomite rich clays from Algarve, Portugal, Applied Clay Science, 42, 2009, pp. 345–355. https://doi.org/10.1016/j.clay.2008.02.008.
- [46] S. Liu, *Rietveld structure refinement of microcline*, European Journal of Mineralogy, 27, 2015, pp. 501–510.
- [47] M.L. Franquelo, M.D. Robador, V. Ramírez-Valle, A. Durán, M.C.J. de Haro, J.L. Pérez-Rodríguez, *Roman ceramics of hydraulic mortars used to build the Mithraeum house of Mérida (Spain)*, Journal of Thermal Analysis and Calorimetry, 92, 2008, pp. 331–335.
- [48] D.T. Griffen, B.T. Johnson, *Strain in triclinic alkali feldspars: a crystal structure study*, **American Mineralogist**, **69**, 1984, pp. 1072–1077.
- [49] R. Palanivel, U.R. Kumar, *Thermal and spectroscopic analysis of ancient potteries*, Romanian Journal of Physics, 56, 2011, pp. 195–208.
- [50] M.S. Tite, Firing temperature determination how and why?, The Aim of Laboratory

Aanalyses of Ceramics in Archaeology, Conference Book, Lund Sweden, April 7-9, 1995, 37-42.

- [51] S. Pavía, *The determination of brick provenance and technology using analytical techniques from the physical sciences*, **Archaeometry**, **48**, 2006, pp. 201–218.
- [52] J. Schomburg, *Thermal reactions of clay minerals: their significance as "archaeological thermometers" in ancient potteries*, **Applied Clay Science**, **6**, 1991, pp. 215–220.
- [53] M.S. Tite, I.C. Freestone, N.D. Meeks, M. Bimson, The use of scanning electron microscopy in the technological examination of ancient ceramics, Archaeological Ceramics, 1982, pp. 109–120.
- [54] S.L. Olsen, *Applications of Scanning Electron Microscopy in Archaeology*, Advances in Electronics and Electron Physics, **71**, 1988, pp. 357–380.
- [55] P. Mirti, L. Appolonia, A. Casoli, *Technological features of Roman Terra Sigillata from Gallic and Italian centres of production*, Journal of Archaeological Science, 26, 1999, pp. 1427–1435.
- [56] M. Maggetti, *Composition of roman pottery from Lousonna (Switzerland)*, British Museum Occasional Paper, 19, 1981, pp. 33–49.
- [57] R.B. Heimann, M. Maggetti, Experiments on simulated burial of calcareous Terra Sigillata (mineralogical change). Preliminary results, British Museum Occasional Paper, 19, 1981, pp. 163–177.
- [58] L.C. Giannossa, T. Forleo, A. Mangone, *The Distinctive Role of Chemical Composition in Archaeometry. The Case of Apulian Red Figure Pottery*. Applied Sciences, **11**, 2021, Article number: 3073. https://doi.org/10.3390/app11073073.
- [59] D. Seetha, G; Velraj, *Characterization and chemometric analysis of ancient pot shards trenched from Arpakkam, Tamil Nadu, India,* Journal of Applied Research and Technology, 15, 2016, pp. 345–353. https://doi.org/10.1016/j.jart.2016.08.002.

Received: January 28, 2021 Accepted: February 20, 2022