



PHYSICS

THE MINERALOGICAL AND MORPHOLOGICAL STUDIES ON ARCHEAOLOGICAL POTTERY SHREDS

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Abstract

The authors are intended to focus the study on archaeological pottery artifacts to characterize the composition in terms of minerals and thereby to estimate the firing atmosphere maintained and firing temperature achieved by the artisans at the time of manufacture for the pottery shreds excavated recently from Sembiankandiyur in India. The scientific techniques FTIR, TG-DTA and SEM-EDS have been employed for the estimation of the firing temperature and conditions by studying the difference in mineral composition in the samples using spectroscopic techniques FTIR analysis. TG-DTA is considered the complementary technique to FTIR analysis in estimating firing temperature by studying the thermal characteristic reactions such as dehydration, decomposition and transformations of minerals in the course of controlled firing of the samples. SEM-EDS studies are concentrated on the morphology and elemental composition of the samples.

Key Words: Artifacts; Firing temperature; FTIR; Mineral transformation; Pottery shred; SEM and TG-DTA.

Introduction

Potteries are the most abundant findings among the archeological artifacts. Pottery analysis reveals information regarding the daily life and cultural aspects of the society of the ancient period (1). Pottery assembles and shreds are frequently studied by researchers in search of information about technological and socio-economical level of past societies. Potteries were made from clay as raw material. In addition the nature and quality of the potteries depend on the firing temperature, firing atmosphere or kiln condition and the technical skill of potters. The technical skills of the ancient potters have been the subject of active research for gaining a deep insight of foregone culture (2). Using spectroscopic technique one can search back the composition and processing which were applied during production time.

The scientific investigation greatly contributes the archeology providing definite and undoubted data about materials, production techniques of potteries to solve the attributed questions. The identification of firing minerals is an essential requirement for the elucidation of firing temperature of potteries. The knowledge of firing temperature and condition of firing give us better

understanding of the civilization that created potteries (3). During firing, the minerals in clays undergo characteristic changes depend upon kiln temperature and condition. A thermal transformation in constituent mineral of clay is considered irreversible. The change in the mineral composition will be observed only if the shred fired above its original temperature applied by the potter. This is the key factor for the investigation of ancient potteries (4). By analyzing the mineral trapped in the sample one can elucidate its firing temperature.

FTIR spectroscopy is considered to be an important tool to analyze the clay minerals and mineral transformation due to thermal effects. Infrared spectra of archeological artifacts reveal the type of clay and temperature of firing (5). Thermal analysis (TGA-DTA) is an adequate tool for analyzing ancient pottery, it allows one to control the process of firing and record variations due to the thermal process simultaneously (6). DTA curves enable detection of exo and endothermic peaks due to the effects of gain/loss of enthalpy occurring in the sample when undergoing controlled heating. Thermal analysis in conjunction with FTIR provides information for

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the estimation of original firing temperature of the ancient pottery (7). Scanning electron microscopy is employed in the morphological characterization of the archeological potteries. SEM provides a high resolution plastic picture with a resolution down to the order about nanometer, which can be interpreted in terms of structural aspects. The SEM picture combined with EDS provides information on the elemental combination in the samples of study.

The present study has been undertaken to estimate the firing temperature and condition of firing of the pottery shreds by analyzing the mineralogical composition, its decomposition upon controlled firing and morphology.

Excavation site

The excavation site Sembiankandiur is located in the Nagappatinam District between northern latitude 11.0851 deg and eastern longitude 79.8545 deg, Tamilnadu, India. The archeological excavation was performed by The State Archaeology Department, Tamilnadu in May 2008 (8). The excavation yielded large assemblages of pottery shred with varied size and style in a trench of dimension 4 by 4 meter and depth of 1.6 m from the surface at the site location. The recovered artifacts were treated conventionally for removing the dirt and stain and categorized. Fifteen samples were procured with the courtesy of State Archeology Department, Tamilnadu. Out of fifteen three shreds were taken as representative samples for the present study by designating them arbitrarily as SKR 1, SKR 2 and SKR 3. The geographical location of the excavation site is given in figure 1.

Fig.1 Geographical map of the excavation site, Sembiankandiur

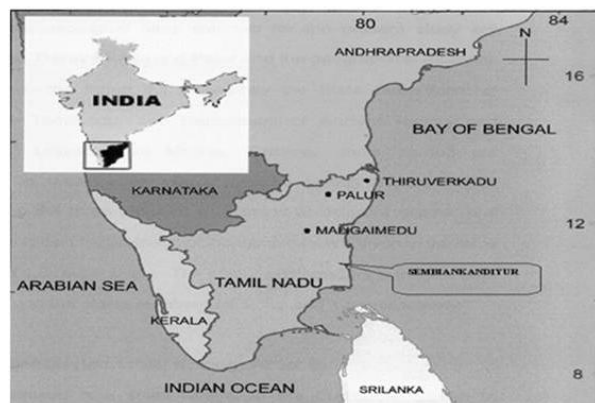


Fig. 2 Photograph of the samples



Visual characteristics of the samples

The photograph of specimens named as SKR 1, SKR 2 and SKR 3 are shown in figure. 2. The shreds are appearing distinctly to each other in respect of color, glaze and thickness. The pot shred SKR 1 is thick walled red coarse ware, probably handmade as the finger impressions are appearing on its surface. The cross section of the fractured shred SKR 1 shows that the margins are red with sandwiching grey core. The sample SKR 2 is red glazed ware, polished on both inner and outer surfaces. The samples SKR 3 is a black colored shred.

Experimental details

FTIR Spectrometry

The infrared spectra were recorded in the mid IR region 4000-400cm⁻¹ using PERKIN ELMER FTIR interferometer in Centralised Instrumentation and Service Laboratory (CISL), Annamali University equipped with Globar source. The KBr pressed pellet technique was used by mixing the powdered samples with KBr in weight proportion of 1: 20. The precision of the FTIR instrument is ± 4 cm⁻¹ in 4000 to 2000 cm⁻¹ region and ± 2 cm⁻¹ between 2000 to 400 cm⁻¹.

Thermogravimetric Analysis:

TGA-DTA study was carried out for the samples SKR 1, SKR 2 and SKR 3 in SDT Q 600 V. 8. 3 Thermal Analyzer with thermal advantage software in Central Electro Chemical Research Institute (CECRI), Karaikudi, India. The experiment was carried out by heating the samples from 30 to 1200° C in steps of 10° C min⁻¹ with flow of high purity Nitrogen.

SEM-EDS

The micrographs were recorded using JSM-5610 LV JEOL model scanning electron microscope combined with EDS operated at an accelerating voltage of 20 kV in secondary electron mode. The shreds were explored by scanning electron microscopy on the fresh fractured face of the samples. To establish the perfect conductivity the specimens were coated with gold and dried in a oven and then micrographs were recorded at the fixed magnification of X500 for all the specimens consistently.

Fig. 3 FTIR spectra of the samples SKR 1, SKR 2 and SKR 3

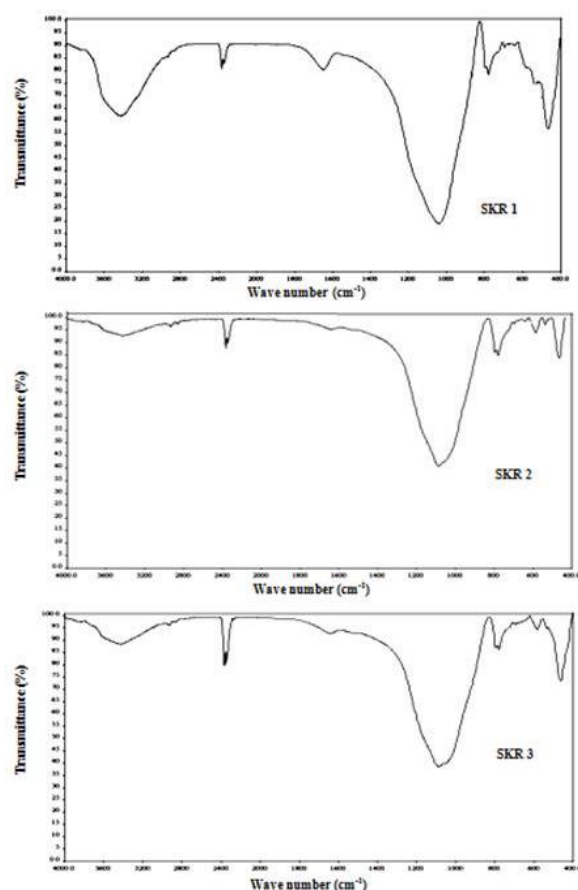


Table.1 FTIR Vibrational Assignments of the Pottery Artifacts

Peak Position Wave number (cm ⁻¹)			Tentative Vibrational Assignment
SKR 1	SKR 2	SKR 3	
3422 S	3421 W	3421 W	O-H stretching
1647 W	1639 VW	1639 VW	H-O-H bending of water
---	1085 VS	---	Wollasonite
1040 VS	---	---	Kaolinite
795 W	796 W	796 W	Si-O quartz
778 W	778 W	778 W	Si-O quartz
694 VW	696 VW	696 VW	Si-O quartz
668 VW	---	---	Anorthite
639 VW	---	---	Si-O-Si bending gehelanite
581 VW	583 VW	583 VW	Fe-O of magnetite
535 VW	535 VW	---	Fe-O of hematite
517 VW	---	---	Fe-O of hematite
465 S	464 M	464 M	Microcline

VS- Very Strong, S-Strong, M- Medium, W-Weak, VW- Very Weak,

Results and Discussion

FTIR analysis

The FTIR spectrum of SKR 1, SKR 2 and SKR 3 are shown in the figure 3. The peak position of various bands of varied intensity observed in these spectra along with their tentative assignments are given in Table. 1. Sankaran and Ramasamy have stated earlier on the IR analysis of archeological artifacts that the absorption band at 3422 and 1639 cm⁻¹ is due to the O-H stretching H-O-H bending of water molecule (9). The presence of absorption band around 3422 and 1639 cm⁻¹ are due to water molecule exists in all samples owing to the absorption of moisture present in the sample. The presence of strong intensity peak at 1085 cm⁻¹ in the spectra of SKR 2 and SKR 3 is the evidence that wollasonite is present in the composition of the shreds, but the absence of corresponding band in the shred SKR 1 is reveals that the shred has no wollasonite in its composition (10,11).

It was reported by Maniyatis and Tite that the band around 1034 cm⁻¹ is due to red clay origin of kaolinite (12). The spectra of SKR 1 has a peak centered at 1040 cm⁻¹ with strong intensity, it indicates that the red clay origin of kaolinite was used in making of the pottery shred SKR 1. The absence of corresponding band in SKR 2 and SKR 3 determines that these shreds are of different origin referring the SKR 1. The appearance of absorption at 795 cm⁻¹ and 695 cm⁻¹ in the spectrum of the samples of the study indicates the quartz presence in accordance with the results of earlier researchers in the similar studies (9). Kieffer stated that the absorption band appearing at 668 cm⁻¹ is due to the presence of anorthite (13). The shred SKR 1 exhibited a weak intensity peak at 668 cm⁻¹ due to clay mineral anorthite and the absence of corresponding peak in SKR 2 and SKR 3 affirms that the SKR 2 and SKR 3 are not having anorthite.

Velraj et al have stated that the absorptions around 580 and 540 cm⁻¹ are due to magnetite and hematite respectively (14). The absorptions observed at 581 cm⁻¹ and 535 cm⁻¹ in SKR 1, 583 cm⁻¹ and 535 cm⁻¹ in SKR 2 are attributed to the magnetite and hematite present in the samples respectively. But the band present at 535 cm⁻¹ in SKR 1 and SKR 2 is not appeared in SKR 3. Therefore it is understood that SKR 3 has no hematite in its composition. The formations of magnetite and hematite depend on the firing atmosphere prevalent at the time of manufacture. The presence of weak intensity peak due to magnetite refers the transformation of Fe₃O₄ to Fe₂O₃ during the firing process. The hematite peak at 535 cm⁻¹ in the samples SKR 1 and SKR 2 implies that the potteries were fired in an oxidizing condition (14). The absence of hematite band in SKR 3 indicates that the

firing condition achieved may be a reduced atmosphere for the sample SKR 3. So it is inferred that the artisans of Sembiankandiyur were well aware of technique of firing the potteries in both oxidizing and reducing atmosphere. The absorption band in all the samples around 465 cm^{-1} is assigned to the presence of clay mineral microcline, referring the studies on fired clay artifacts by Farmer (15).

The firing temperature of potteries

According to Ahlem Chakchouk et al and Shoval the decomposition of kaolinite and formation of meta kaolinite occurs around 500 to 650°C (16,17). The appearance of kaolinite in SKR 1 suggests that the firing temperature was not high enough to complete the decomposition of this mineral indicating that the firing did not exceed 650°C . Ramaswamy and Kamalakannan have stated that the IR absorption band at 915 cm^{-1} is due to $\text{Al}(\text{OH})$ vibrations in octahedral sheet structure which begins to disappear at the temperature 500°C (18). The shreds in the present study have no band at 915 cm^{-1} . So it is viable to understand that all the samples were fired above 500°C . The presence of kaolinite and the absence of $\text{Al}(\text{OH})$ vibrations in the spectrum of pottery SKR 1 show that its firing temperature lies between 500 to 650°C .

The absorption peaks at 1085 cm^{-1} , 583 cm^{-1} and 464 cm^{-1} in SKR 2 and SKR 3 are due to the clay minerals wollastonite, magnetite and microcline present in the matrix of the samples. According to Shoval the firing temperature 800°C is sufficient to decompose the calcite (17). Lara et al have stated that the magnetite is formed at a temperature 800 - 850°C (19). The presence of magnetite and the absence of calcite in the shreds SKR 2 and SKR 3 indicates that the samples were fired above 800°C . According to Barilaro et al wollastonite originate from chemical reaction between quartz and carbonates when the temperature reaches 900°C (20). The presence of magnetite, wollastonite and the absence of calcite in SKR 2 and SKR 3 indicate that the samples were fired between 800°C to 900°C .

Thermal analysis

The TGA and DTA curves are shown in the figure 4 for the shreds individually. The DTA curve for each sample shows both exo and endothermic peak at different temperatures due to distinct nature and composition. According to Clark et al and Moropoulou et al, the endothermic peak around 100 to 200°C is due to the hygroscopic water (7,21). For SKR 2 an endothermic peak due to hygroscopic water molecules was observed between 30 to 250°C , whereas for SKR 1 and SKR 3 an exothermic peak was observed between 30 to 100°C indicating the absence of hygroscopic water. According

to Clark et al the exothermic peak between 200 to 500°C is due to the combustion of organic material present in the sample (7). A broad exothermic peak appeared between 205 - 500°C in SKR 2 is due to the combustion of organic material and this peak was not present in SKR 1 and SKR 3. So the shred SKR 2 has some organic material associated with the clay of the shred. The organic material might be added intestinally as a binder in the preparation of pottery or the raw material itself has contained organic material (21).

Fig. 4 Thermal curves of the pottery shreds SKR 1, SKR 2 and SKR 3

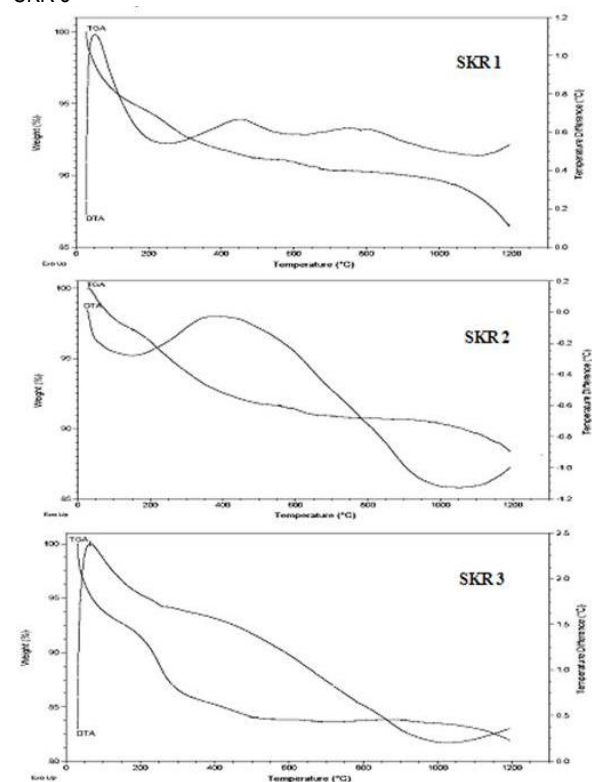


Table. 2 Weight Loss From Thermogravimetric Curves Of The Samples

Shred code	Weight loss			weight loss	Residual mass	Total weight loss
	Dehydration (room temperature 30 to 200°C)	Decomposition of hydroxyls (400 - 500°C)	Decomposition of calcite (700 - 800°C)			
SKR 1	5.63 %	1.11 %	0.2 %	(50 - 495°C)- 8.78 %	86.42%	13.58 %
SKR 2	1.38 %	1.31 %	0.11 %	(50 - 650°C)- 8.8 %	88.35%	11.65 %
SKR 3	8.69 %	1.85 %	0 %	(50 - 500°C)- 15.96 %	81.95%	18.05 %

Ahlem chakchouk et al and Mohamed Hajjaji et al have stated that the endothermic peak appearing between 450 to 650°C is due to the dehydroxylation of kaolinite [16,22]. In SKR 1 the presence of kaolinite is well evidenced by endotherm between 450 - 650°C . It

indicates that the kaolanite mineral has survived in the firing process applied by the ancient potter. According to Foss Leach et al the presence of dehydroxylation kaolanite peak is the indication that the pottery is not fired above 650°C [23]. Therefore, the shred SKR 1 would have been fired between $450 - 650^{\circ}\text{C}$. But the absence of the corresponding endothermic peak both in SKR 2 and SKR 3 between the temperatures $450 - 650^{\circ}\text{C}$ indicates that shreds were fired at temperature above 650°C . The absence of exothermic peak between $900 - 1000^{\circ}\text{C}$ on the fired clay products stands for evidence that products were not fired above the higher limit of the temperature [7]. As no samples of the study has exothermic peak between $900 - 1000^{\circ}\text{C}$ gave a clue that all the samples were fired around or below 900°C .

In the thermogravimetry analysis the weight loss observed on the pottery samples can be explained in three steps referring the results reported by Drebushchak et al [6].

1. The dehydration (Room temperature 30 to 100°C)
2. Decomposition of hydroxyls ($400 - 500^{\circ}\text{C}$)
3. Decomposition of carbonates, mainly calcite ($700 - 800^{\circ}\text{C}$).

Data on the thermal decomposition of three samples are summarized in table 3. The mass loss on temperature intervals is not uniform in the samples of the study in mineral composition of pottery shreds. For all the shreds mass loss in dehydration is larger than the loss in dehydroxylation. The weight loss due to dehydration of water is 5.63% , 1.83% and 8.69% for the shreds SKR 1, SKR 2 and SKR 3 respectively. But the weight loss due decomposition of hydroxyls is not showing much variations relatively and it varied from 1.11 to 1.85% among the samples of the study. The sample showed weight loss from 0 to $.02\%$ due to decomposition of calcite which occurs in the temperature range $700 - 800^{\circ}\text{C}$ indicating the samples has no calcite in its composition. The absence of thermogravimetric evidence of calcite between $700 - 800^{\circ}\text{C}$ is supporting the result of the FTIR analysis done in the present study.

The shred SKR 1 showed maximum weight loss from 50 to 495°C , the weight loss in this region is 8.53% of total weight loss 13.85% and it is due to loss of moisture water and loss of water from iron hydroxyls, which has been identified through the endothermic peak in DTA appeared between 150 to 350°C (21). The total weight loss in SKR 1 up to 1200°C is 13.58% and the higher weight loss observed in the temperature region 50 to 650°C is 8.8% . This weight loss is due to dehydration accompanied by combustion of organic materials. The weight loss due to organic material is alone 3.80% between the range 200 to 500°C . The total weight loss

through the entire thermal analysis is 11.65% . In shred SKR 3 the total weight loss is 18.05% and the maximum weight loss is occurred in the region of temperature $50 - 500^{\circ}\text{C}$ of about 15.96% .

SEM-EDS Analysis

Fig.5. The EDS spectrum of the shreds SKR 1, SKR 2 and SKR 3

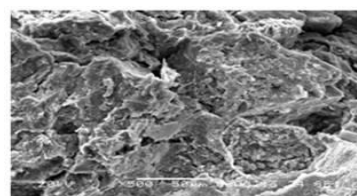
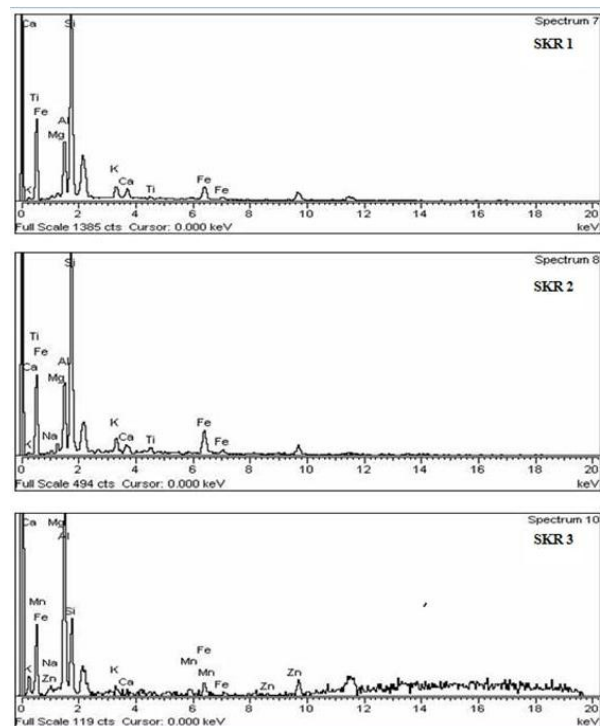


Fig. 6 SEM Micrographs of the shred SKR 1

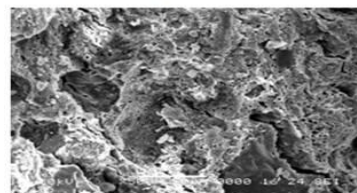


Fig. 7 SEM Micrographs of the shred SKR 2

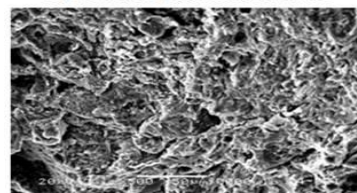


Fig. 8 SEM Micrographs of the shred SKR 3

Table 3. Elements present in the pottery shreds of study

Elements		Elemental concentration weight (%)		
		SKR 1	SKR 2	SKR 3
Sodium	Na	----	1.27	0.41
Magnesium	Mg	1.39	2.09	0.53
Aluminum	Al	14.35	14.25	44.06
Silicon	Si	56.55	51.05	30.20
Potassium	K	5.76	4.92	3.07
Calcium	Ca	5.03	2.71	1.24
Iron	Fe	15.48	21.11	13.87
Titanium	Ti	1.44	2.60	0

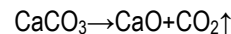
The EDS spectrum of the samples were shown in the figure.5. Elemental composition in weight percentage of the pottery samples were given in the table.3. The major constituent elements of potteries were silicon, aluminium and iron and the other elements magnesium, potassium, calcium and titanium were present in low weight percentage. The variation in percentage of elements between specimens SKR 1 and SKR 2 is not significant, whereas SKR 3 showed significant difference in percentage of Si (30.20 %) and Al (44.06 %) respectively.

The elements such as iron, magnesium, aluminium and potassium were identified in the EDS of SKR 1, SKR 2 and SKR 3 and it was inferred that they would have acted as fluxes during firing to produce stable glaze (24). EDS analysis showed the presence of iron and calcium contents in all the samples. Iron oxide imparts red colour to shreds during firing. Iron within the sample plays a vital role to give coloring on the pottery during firing process and also depends on the presence of oxygen content in the atmosphere. Calcium is a significant ingredient at high temperature to give glaze to the potteries (25).

The morphology of the shreds SKR 1, SKR 2 and SKR 3 are shown in figures 6 to 8. Though the samples were procured from the same trench, the morphology of the three shreds differ distinctly. The morphology of the shred SKR 1 appeared volumetric plate like grains with no internal pores in the structure. The similar morphological structure was observed by Krapukaityte et al and they have interpreted that the shred was fired at low temperature (26). It allowed us to infer that the shred SKR 1 might be fired relatively at low temperature.

The shred SKR 2 shows a broad distribution of irregularly shaped agglomerates with pores of size less than 10 μm . According to research reports found in the review of literature it may be us interpreted that the specimen was fired using multi step technology (27). The micrograph of SKM 3 showed granular structure composed of irregularly aligned grains with voids of arbitrary shapes from 5 to 10 μm in dimension and few pores are also observed. The pores in SKR 2 and voids in SKR 3 should have been formed by the escape of gases during the fabrication process. The presence of calcite in the fired clay artifacts is the indication that they

were fired at a temperature above 850° C. The thermal reaction of CaCO_3 to decompose into CaO and gas CO_2 is given below



Traore et al have found and explained the formation of pores in the morphology of pottery as a result of CO_2 exhaust on the decomposition of CaCO_3 (28). So the pores and voids in SKR 2 and SKR 3 might be formed from the escape of CO_2 gas from the pottery during the decomposition of calcite during the firing process. According to Christina Papachristodoulou et al calcite decomposes at 850° C (29). So, the shreds SKR 2 and SKR 3 might have been fired around 850° C. The range of firing temperature estimated by the SEM morphology is in agreement with the FTIR studies as a part of the investigation.

Conclusion

Ancient pottery samples were characterized by FTIR, TG-DTA and SEM analysis. The results of the analytical techniques on firing temperature estimation are complementary with one another. From the vibrational analysis two samples SKR 1 and SKR 2 are identified that they have been fired in an oxidizing condition, whereas SKR 3 would have been fired in a reducing atmosphere. The TGA-DTA thermal data are also supporting the FTIR observation on estimating the range of firing temperature achieved by the artisans for the shreds SKR 1, SKR 2 and SKR 3 respectively. The SEM with EDS data are characteristically confirm the percentage of elements present in the pot shreds and complement the range of firing the temperature achieved by the artisans on the shreds of study.

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