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Vibrational Spectroscopy

Elixir Vib. Spec. 79 (2015) 30451-30454

ISSN: 2229-712X

Spectroscopic analysis of archaeological pot shreds recently excavated from Alagankulam,Tamilnadu, India

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ARTICLE INFO

Article history:

Received: 16 December 2014;

Received in revised form:

25 January 2015;

Accepted: 14 February 2015;

Keywords

FT-IR spectroscopy, XRF, XRD,

Firing techniques (firing temperature and atmosphere),

Pot shred,

Alagankulam (Tamilnadu).

ABSTRACT

Alagankulam region covering Tamilnadu in Southern India has numerous cultural heritages due to its witness to various social movements of different civilizations in ancient times. Archaeological excavations carried out at different depths of the trench revealed the most significant findings of pot shred, roulette ware and amphorae jar pieces and pieces of red ware etc. These relics are dated back to 3rd - 4th century. In this study, pot shred of grey ware unearthed from Alagankulam site were investigated by FT-IR spectrometry. Energy dispersive X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses were used as complementary techniques in order to expose chemical and mineralogical phase contents respectively. Obtained results showed that these potteries have been produced with non-calcareous clays and include moderate amounts of MgO, K_2O, Na_2O and Fe_2O_3 in this context. Additionally, high temperature phases have also been detected with XRD analyses in some samples.

Introduction

Archaeology is the scientific study of material remains of past human life and activities. These include human artefacts from the very earliest stone tools to the man-made objects that are buried or thrown away in the present day. Archaeological investigations of representative exhumed areas are the principal source of modern knowledge of prehistoric, ancient and extinct cultures [1]. Alagankulam site has witnessed crucial changes, innovations and developments throughout the history mostly due to its location in Tamilnadu where is situated within the delta basin of the river Vaigai, just 18 kilometres from Ramanathapuram city on the way to Rameswaram. As a consequence of this, there are numerous ancient settlements and materials waiting to be investigated.

The most remarkable materials of such relics are potsherds of Mediterranean origin, Roman coins of Valentine II, Arcadias and Theodosius II, pot shred with Roman ship graffiti, shred with two lady figurines identified with Egyptian origin, Tamil brahmi sherds with Ceylon brahmi script found and an ancient Roman port. The collected artefacts revealed Indo-Roman trade contact and are assignable to the first century BCE [2].

In scientific researches, there are many various characterization methods applied on especially ancient ceramic materials in order to investigate the specific characteristics of their structural features. In this sense, some of the conventional characterization techniques are X-ray fluorescence (XRF) and X-ray diffraction (XRD), scanning electron microscopy (SEM) with wavelength or energy dispersive X-ray spectrometry (WDX/EDX), Mossbauer, Fourier transform infrared (FTIR) and Raman Spectroscopy [3-9]. These techniques provide identification of mineralogical/phase composition which initially depends on raw materials, production technologies and burials conditions. Additionally, since the minerals are evidences of formation and decomposition of solid phases occurred during firing, duration of firing, maximum temperature reached and atmospheric conditions of firing process are the significant parameters in estimating and considering the changes in ceramic fabrics which will then enlighten the secrets about ancient samples [10, 11].

Fig.1. Location of Alagankulam (almost 18km to Ramanathapuram)

While investigating ancient artefacts, one of the most important subjects is mineral identification. In this sense, minerals which are expected to be defined in archaeological ceramic residues can be considered in three stages, namely; “primary minerals” that are already present in used raw materials, “secondary minerals” that occur during use and burial

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of historical findings, and "firing minerals" that are formed during firing process [11-14].

This approach would be directive to reach proper results in terms of estimating provenance and production techniques of potsherd samples uncovered from archaeological excavations.

The aim of this study is to characterize ancient potteries found in the various layer encountered in archaeological excavations in Alagankulam (Tamilnadu) (Fig.1) by using Fourier transform infrared (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The last two analyses are used as complementary techniques to define chemical and mineralogical/phase contents, respectively. After gathering all the results obtained by these techniques, it would be possible to reveal production technology (especially firing techniques) and mineralogical components of potsherds of the site which is dated back to Early- historic times (approximately from half of the 4th millennium BCE).

Materials and Methods

Archaeological Samples

Among 75 relics from Alagankulam (Lat. 9° 21' N; Long. 78° 58' E) five pot shred which belong to different depths of the trench were selected for the study. These samples have the colours of grey and white. Some of them have traces of ornamentation including floral or figurative decorations. Images of potteries are given in Fig.2. Types of the samples are rim, edge, neck and handle of the ceramic wares.

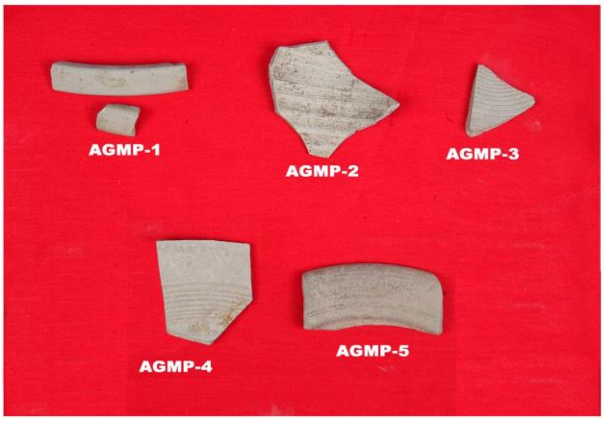

Fig.2. Image of Alagankulam potsherd

Methods

The samples were ground in an agate mortar into fine powder for FT-IR, XRD and EDXRF analysis. Bruker S4 – Pioneer instrument was used for chemical analysis of major and minor elements. Pellets consisting of 4mg sample powder and 80mg binder (KBr) were prepared by pressing process with a pressure value of 10 tones. XPERT-PRO powder diffractometer with CuKα radiation and JCPDS software were used for the mineralogical analysis. The patterns of XRD were obtained by scanning 3–80^o 2θ, with a goniometer speed of 2^o/min. Perkin Elmer RX1 spectrometer (with 4 cm^{-1} resolution) possessing KBr beam splitter was used to collect IR spectra of the samples. The scan range was 4000-400 cm^{-1} and wave number of IR-Laser was 15798.00 cm^{-1}.

Results and Discussions

EDXRF and XRD Results

When EDXRF results are examined from Table.1, CaO quantities change between 0.71 and 1.77 wt.%. So, this indicates that the potteries may have been produced by using non-calcareous clays [15]. MgO and K_2O quantities are in moderate range of 0.41-2.70 and 4.23-4.89 wt.%, respectively. Na_2O quantities change between 0.49 and 0.98 wt.%. Iron oxide (FeO) quantities change between from 4.80 to 8.86 wt.%. In context of mineral diversity; quartz (SiO_2), feldspars [albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$)], mullite ($3Al_2O_3.2SiO_2$), illite (K,H_3O) (Al,Mg,Fe)$_2$ (Si,Al)$_4O_{10}$ [(OH)$_2$,(H_2O)], muscovite ($KAl_2(AlSi_3O_{10})$ (F,OH)$_2$), hercynite ($FeAl_2O_4$) and hematite (Fe_2O_3) were identified from XRD spectra of potsherds (Table.2) [16].

Table.1 EDXRF results of potsherds
(A represents AGMP; i.e. A1= AGMP 1)

Oxide (wt.%)	Sample Code				
	A1	A2	A3	A4	A5
SiO_2	58.380	67.940	59.380	60.520	62.020
Al_2O_3	20.600	20.160	19.920	20.560	19.770
FeO	8.758	4.800	8.869	8.277	7.210
MgO	2.598	0.411	2.484	2.608	2.703
CaO	1.772	0.717	1.540	1.020	1.400
Na_2O	0.683	0.497	0.888	0.980	0.752
K_2O	4.592	4.234	4.891	4.613	4.690
TiO_2	0.911	-	0.988	0.921	0.936
P_2O_5	1.270	-	0.671	0.197	0.255
Cr_2O_3	0.024	-	0.023	0.022	0.022
Rb_2O	0.020	-	0.017	0.016	-
SO_3	0.059	0.100	0.061	0.048	0.059
ZrO_2	0.012	-	-	-	-
MnO	0.114	0.158	0.118	0.088	0.057
BaO	0.140	0.143	-	-	-
CuO	0.015	-	0.015	0.013	0.015
NiO	0.010	-	0.012	0.010	-
SrO	0.029	0.804	0.019	0.014	-
ZnO	0.020	0.026	0.016	0.015	0.016

Table.2 XRD results of samples

Sample Code	Minerals/Phases
AGMP-1	Quartz, Muscovite, Hercynite
AGMP-2	Quartz, Mullite, Hematite
AGMP-3	Quartz, Albite, Muscovite, Hercynite
AGMP-4	Quartz, Illite, Hematite
AGMP-5	Quartz, Orthoclase, Muscovite/Illite, Hematite

FT-IR Results

FT-IR analyses were carried out in range of 4000-400 cm^{-1}, because this range is the finger-print area indicating the required information for clay mineral evaluations. FT-IR spectra of selected representative potsherd samples (AGMP-1 to AGMP-5) are given in Fig. 3 and their tentative vibrational assignments are established in Table 3. These specimens have been chosen according to diversity of their XRD phases.

The spectrum of AGMP-1 indicates to quartz (797 cm^{-1} and 778 cm^{-1}), kaolinite (1075 cm^{-1}), and feldspar (648 cm^{-1}) [17,18]. XRF analysis of AGMP-1 revealed moderate amounts of SiO_2, Al_2O_3 and Fe_2O_3, and very low amount of CaO, so these results have been related with FT-IR results. Additionally, XRD pattern of AGMP-1 has also revealed the presence of quartz, hercynite and muscovite. Consequently, absence of hydroxyl band of kaolinite and high temperature phases and presence of silicate at higher wave number region allow us to estimate the firing temperature greater than 800^{o}C, because structural decomposition of kaolinite is completed at this temperature range [19].

According to FT-IR results of AGMP-2 the most obvious peaks belong to quartz (796 cm^{-1}, 778 cm^{-1} and 694 cm^{-1}) [19]. In accordance with the references, spectrum of AGMP-2 indicates to amorphous aluminosilicates (1084 cm^{-1}), and hematite (535 cm^{-1}) [20]. But, these results are considered by only characteristic band ranges of the minerals that take place in literature. Thus, they should be interpreted with contribution of chemical and mineralogical analysis.

In this sense, as the XRD pattern of this pottery points to existence of quartz, mullite and hematite minerals; 555 cm^{-1} is likely to indicate to presence of mullite and are related with formation/decomposition reactions of the kaolinite, and it is formed above 800^oC with the reaction of kaolinite → metakaolinite → γ-Al_2O_3 → mullite structure [21].

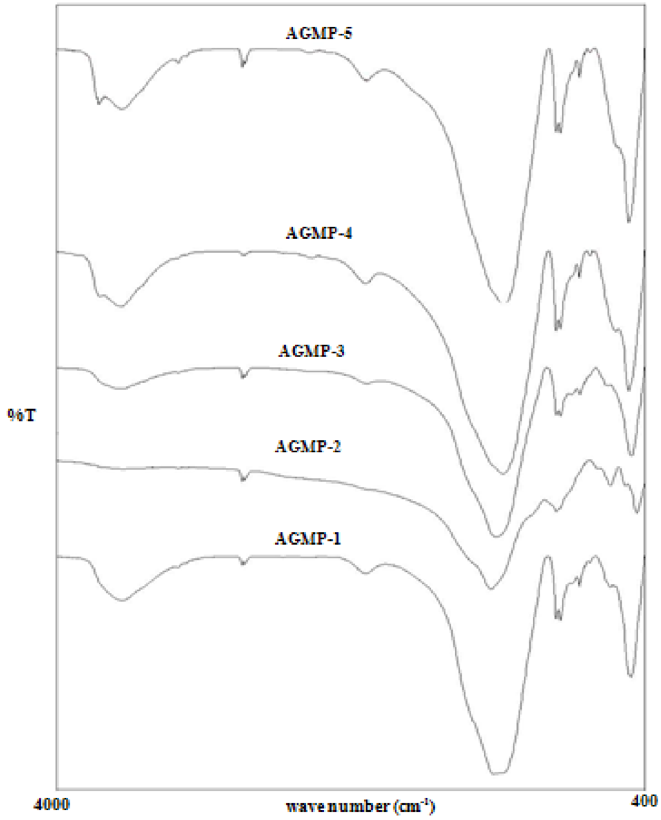

Fig 3. FT-IR spectra of Alagankulam pot shred

Table 3. IR absorption frequencies (cm^{-1}) and tentative vibrational assignments of Alagankulam pot shred

Pot shred code – IR bands [wave number (cm^{-1})]					Tentative vibrational assignments
AGMP-1	**AGMP-2**	**AGMP-3**	**AGMP-4**	**AGMP-5**	
-	-	-	-	3700 VW	O-H str. of external hydroxyl group of kaolinite
-	-	-	-	3648 VW	O-H str. of external hydroxyl group of kaolinite
-	-	-	3618 VW	3620 VW	O-H str. of inner hydroxyl group of kaolinite
3421 VW	3426 VW	3427 VW	3420 VW	3424 VW	O-H str. of adsorbed water
1636 VW	1630 VW	1628 VW	1634 VW	1628 VW	H-O-H bending of adsorbed water
1075 S	1084 M	1080 M	-	-	Al-Si-O str. of amorphous aluminosilicates
-	-	-	1033 VS	1027 M	Si-O str. of clay minerals
797 W	796 W	796 VW	797 W	796 W	Si-O symmetrical str. of quartz
778 W	778 W	778 W	778 W	778 W	Si-O symmetrical str. of quartz
-	-	731 VW	-	-	Al-O-Si str. of feldspar
694 W	694 W	693 VW	694 W	694 W	Si-O symmetrical bending of quartz
648 VW	-	-	647 VW	648 VW	Al-O-Si str. of feldspar
568 VW	-	567 VW	-	-	Fe-O of hercynite
-	555 VW	-	-	-	Al-O-Si str. of mullite
-	535 W	-	534 W	536 W	Fe-O bend of hematite
466 M	464 W	467 W	467 M	467 S	Si-O-Si bending of silicates

Relative Intensity: VW - very weak, W - weak, M - medium, S - strong, VS - very strong

FT-IR spectrum of AGMP-3 is dominated with aluminosilicate band (1080 cm^{-1}) [17, 18]. The results also include quartz (780 cm^{-1}) feldspar (731 cm^{-1}) and silicates (467 cm^{-1}) [20]. XRD pattern of AGMP-3 approves the existence of quartz, albite, muscovite and hercynite and chemical analysis of the potsherd also shows that the highest amount of SiO_2 and low CaO takes place in this specimen. Consequently, all results of these characterization techniques have suggested that this pottery has been produced by non-calcareous clay and this raw material may include low amount of feldspar/plagioclase and illite/muscovite.

The infrared spectrum of AGMP-4 and AGMP-5 indicates to kaolinite (~1030 cm^{-1}), quartz (797, 778 cm^{-1} and 694 cm^{-1}), feldspar (647 cm^{-1}) and hematite (~530 cm^{-1}) [17, 18, 20]. XRD pattern of AGMP-4 and AGMP-5 clearly shows the presence of quartz, orthoclase, illite and hematite but in XRD pattern, due to absence of crystalline structure with rise in temperature, it is not possible to consider the kaolinite mineral through X-ray spectrum. Nevertheless, bands at 1030 cm^{-1} and 1080 cm^{-1} in the spectrum may be attributed to existence of silicates which is another member of clay minerals. But, this estimation may be accurate after gathering chemical and mineralogical analyses with infrared spectra. As a result of these data; firing temperature of these two ceramic samples is likely to be less than 800^oC at which there is a occurrence of kaolinite hydroxyls and absence of high firing minerals with the increase of temperature [19].

Conclusions

This study, in which infrared spectroscopy is used together with XRD and EDXRF to characterize the samples of ancient potsherds found in the archaeological site of Alagankulam (Tamilnadu) India, gives the opportunity to determine technological conditions of pottery production in the region in ancient times.

The obtained results indicate that potsherds from the ancient port city Alagankulam were primarily produced with clay deposits poor in calcareous materials. Mineralogical compositions of the potsherds suggest that potteries should have been exposed to different firing temperatures during sintering process. Presence of mullite (in AGMP-2) and aluminosilicates (in AGMP-1 and AGMP-3) allows us to make an interpretation that the firing temperature of these two samples should not be less than 800^oC due to formation conditions of aforementioned high-temperature phases.

Firing temperature of other potteries should not be higher than 600^oC-700^oC due to presence of mainly kaolinite clay mineral and absence of high firing phases. Although any ceramic kiln has not been recovered in the excavation area so far, it is not exactly precise that there is not a firing place in the settlement layers.

Except from AGMP-1 and AGMP-3, other potsherd samples mainly adopted open firing. All these information have been detected by infrared spectroscopy by comparing characteristic band ranges of the hematite minerals.

This provide us to draw a conclusion that people have used non-calcareous clays as their raw materials, since this type of materials could provide them the opportunity of keeping shape of the product after forming process and were abundant in the region.

Acknowledgments

The authors acknowledge with thanks to the State Department of Archaeology, Chennai, for providing the archaeological samples for this work. The authors also thank to The Professor and Head, Department of Physics, Alagppa

University, Karaikudi, The Head, Centralized Sophisticated Instrumentation Lab (CSIL), Annamalai University, Annamalai Nagar and Elisa Fathima, The Staff-in-charge, Centralized Instrumentation Facility (CIF), Pondicherry University for granting permission to record XRD, FT-IR spectra and XRF spectra, respectively.

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