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Research Article

Determination of Firing Techniques of Ancient Artifacts by using FT-IR Analysis

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Abstract

The effects on ceramic products of firing conditions, firing temperatures are assessed here through mineralogical composition by the FT-IR technique. Ancient potteries are the representative tool for material culture that results in the interaction between man and his territory. The FT-IR spectra were recorded in the mid IR region 4000 to 400 cm^{-1}. An attempt has been made to reveal the clay mineral constituents and clay origin of the remnants from the positions of IR absorption bands with their relative intensities and the respective tentative vibrational assignments are assigned with available literatures. Through the mineralogical compositions the firing techniques (firing temperature and firing atmosphere) of the artifacts are measured. The ancient artifacts were collected from Vadamangalam and Pondur sites in Sriperumbuthur district, Tamilnadu.

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Introduction

Within archaeological artifacts there is a record to which an archaeologist is blind but which physicists can hope to read. To be able to read and analyze archaeological or historical artifacts, we need to probe the mineral composition of the matter to determine its firing techniques. This requires non-destructive method as FT-IR spectroscopy for material analysis. The science methods are used for probing forgotten and lost history of mankind. Archaeology is 'the science of the artifact' and every vessel carries the information about past society. Such relics are potteries, bricks and tiles etc.

Pottery always reflects contemporary tastes and cultural ideals and so it is an ideal subject of art-historical study. Different shapes and decorations were used at different times, by different people, and for different purposes. So by studying pottery, archaeologists can date their sites and say a great deal about ancient cultures. It provides information about technology, craft specialization, trade, industry, art, diet and a host of other attributes of ancient cultures. When clay is fired the structure of the minerals is destroyed forever, and they become a glassy mass. This fixes the pottery in its shape permanently. There are three main types of fired-clay ceramic. Earthenware is a relatively low-fired clay ceramic (about 700-1200^{o}C), stoneware is fired to a higher temperature (about 1200-1300^{o}C) and porcelain is a highly fired ceramic (about 1300^{o}C). There are various types of clay mineral, and not all can be fired at higher temperatures.

There are two different ancient firing techniques are i) pit firing, a technique in which pots were placed in an open pit, covered by straw and wood, fired and then covered with earth in order to preserve heat and increase the firing temperature; ii) kiln firing, a more highly developed technique, for which permanent or partially permanent structures were used, and in which the fire was separated from the pots by the chamber. The varying arrangement and location of pots with respect to the fire result in significantly different firing conditions. Pit firing has a high heating rate (tens of degrees per minute), short residence time (maximum temperature maintained constant for a certain period of time) (a few minutes), and reducing conditions, excluding vessel deliberately exposed to the air while still at high temperature [1,2]. In kiln firing, the heating rate is generally low (a few hundreds of degrees per hour), residence time is long (many hours), and redox conditions may vary depending on the type of kiln, although they vary generally oxidizing [1, 2].

In the present work, the FT-IR analysis made to elucidate the clay mineralogy of antique relics. The clay mineralogy exploited to obtain the firing technology, which is used to know the technical knowledge of artisans.

Excavated site and the Sample details

Sriperumbudur is in the Indian state of Tamil Nadu located 40 km west south-west of the city of Chennai. It is famous for being the birthplace of Sri Ramanuja, one of the most prominent Hindu Vaishnava saints as well as the town where former Indian Prime Minister Rajiv Gandhi was assassinated in 1991. The old name of Sriperumbudur is Bhoodhapuri. It is believed that the doors of heaven will be open for those who die at Sriperumbudur.

For the present investigation ceramic artifacts are recently unearthed from two different archaeological sites namely Vadamangalam and Pondur, Sriperumbuthur district in Tamilnadu, India on March 2013. The six samples of interest are approximately dated back to 2^{nd} centuries AD to 3^{rd} centuries BC. The collected samples were named as VDMP1, VDMP2, VDMP3, VDMP4 and VDMP5 for Vadamangalam samples are shown in Fig. 1. The Pondur sample PDR and the top view of PDR sample is shown in Fig. 2 to exhibit the black and red part of the shard. All the samples are red ware and red and black ware are given in **Table 1**.

Table 1 Description of Vadamangalam and Pondur artifacts

S.No	Sample code	Depth (cm)	Physical characteristics
1	VDMP1	25	Red ware
2	VDMP2	25	Red ware
3	VDMP3	25	Red and black ware
4	VDMP4	25	Red ware
5	VDMP5	25	Red ware
6	PDR	25	Red and black ware

Experimental techniques

FT-IR spectra were recorded in the mid infrared region (4000-400 cm^{-1}) in an evacuated chamber of **Bruker Tensor 27** spectrometer using KBr discs as matrices. The spectral resolution is 2 cm^{-1} was used and the spectra were accumulated over 16 scans. The FT-IR spectroscopy applied for all the samples. The sample mixed with KBr in the ratio of 1:20. At first the sample is crushed and ground with KBr. The mixture of grounded sample and KBr was pelletized as disc. The fitting of peaks and smoothing were done by the OPUS 6.5 software in the instrument over the working window, 4000-400 cm^{-1}.

Results and Discussion

The mineral compositions of the ceramic samples were analyzed by the FT-IR spectra given in Fig.3 & Fig.4. The IR absorption band intensity and the corresponding vibrational assignments were publicized in **Table 2- Table 3**.

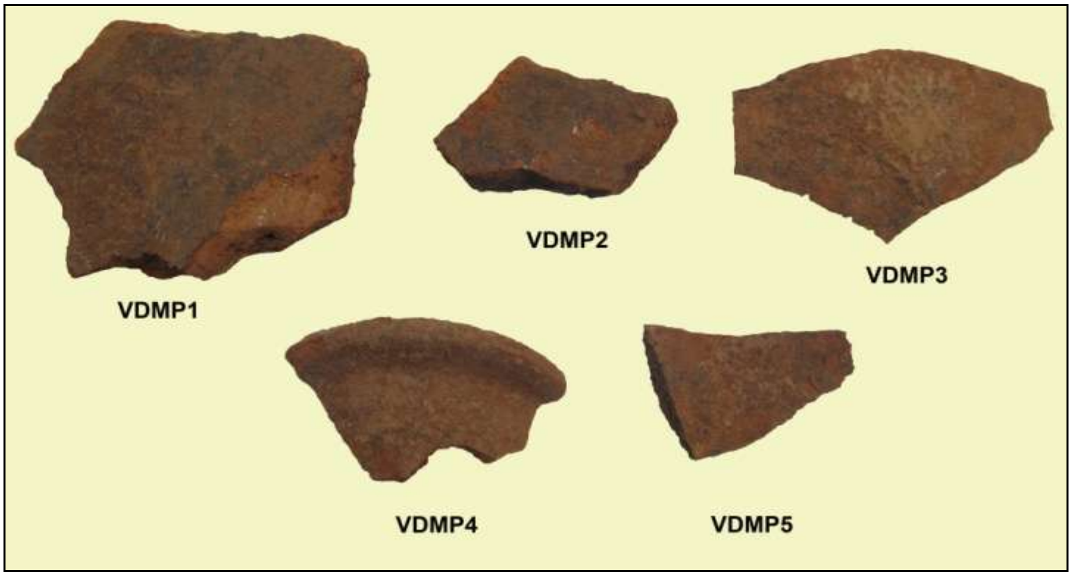

Figure 1 Photograph of Vadamangalam (VDMP1-VDMP5) shards

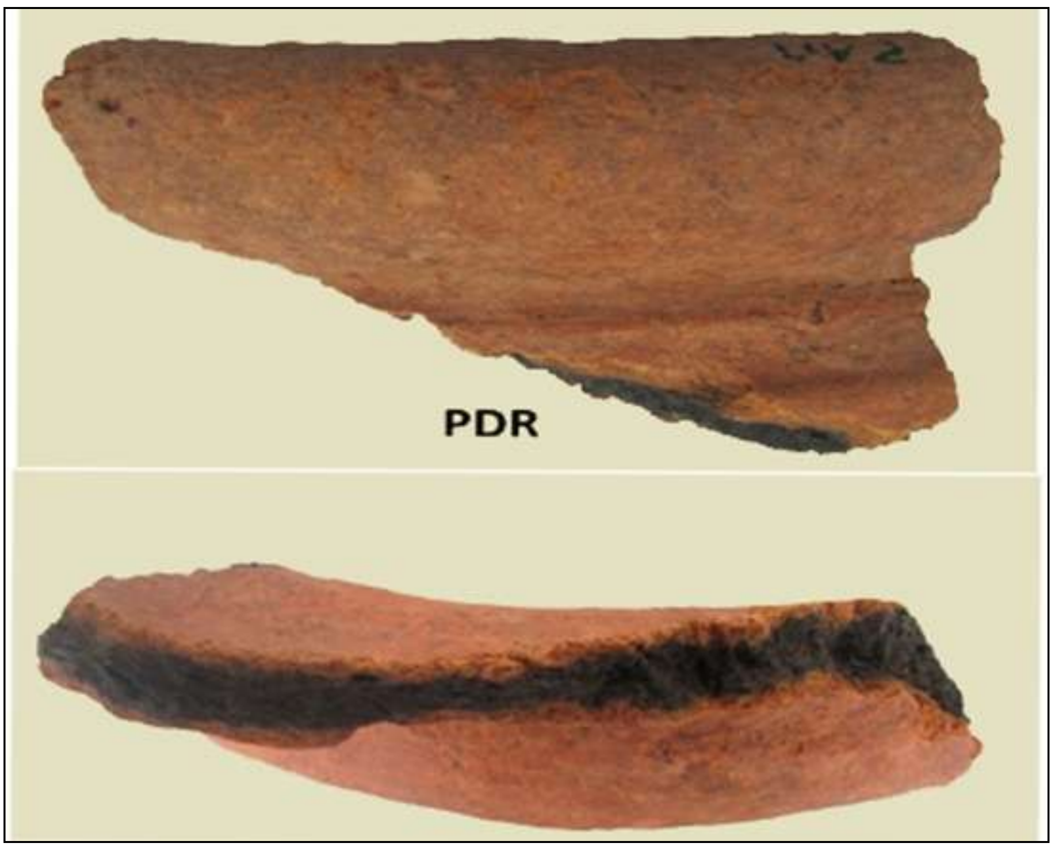

Figure 2 Photographs of Pondur (PDR) shards and its Top view

Vadamangalam (12º 57"N, 79º 56"E) site

The absorption bands observed at 3420-3445cm^{-1} and 1620-2642 cm^{-1} could be assigned to the OH stretching and H-O-H bending of water molecule, which is observed in almost all the natural silicates [3-5].

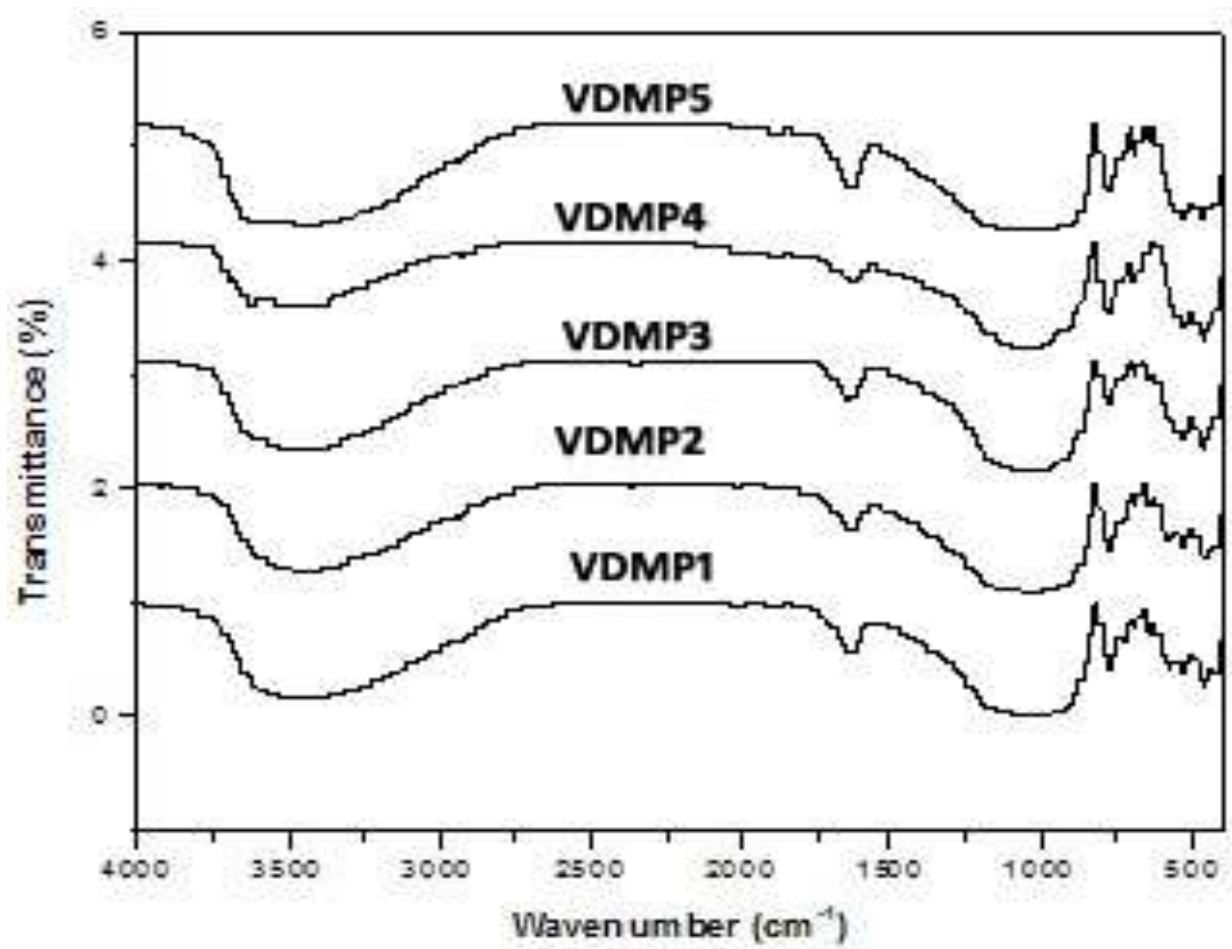

Figure 3 FT-IR spectra of Vadamangalam pot shards (VDMP1-VDMP5)

The very strong intensity IR band centered around 1033-1037 cm^{-1} along with 1014 cm^{-1} in all the artifacts may be assigned to Si-O stretching of kaolinite and is the result of red clay origin [3]. Kaolinite dehydroxylates and transforms to metakaolinite at about 450–650˚C [6, 7]. This declares that all the samples may be fired below 650˚C. None of the samples taken for the present study showed the sharp shoulder band at 915 cm^{-1}. This implies that all the samples were fired to the temperature above 500˚C [8]. Both of these bands are tells that all the pot shards were fired between 500-650˚C.

According to Ramasamy et al. (2009), the strong intensity bands at around 777 and 692 cm^{-1} contains Si-O stretching of quartz [9]. The weak Al-O-Si stretching of feldspar was present in all the pot shards are allocated to 644-647 cm^{-1} except in the VDMP4 [10]. The medium intensity absorption band at 578 and 581 cm^{-1} indicative of magnetite is only in the VDMP1 and VDMP2. The hematite was present in all the samples represent to 535 cm^{-1} and the intensity is very strong to medium [11-15]. The amount of magnetite and hematite decides the oxidizing or reducing atmosphere for firing the artifacts respectively [14, 16–18]. The method of firing is very essential rather than temperature numbers, as temperature in general is extremely unstable and variable through time and space, within a structure and even on a single vessel [19, 20]. In our case, hematite is affluent in all the samples, which is seems to be red color. The less amount of magnetite is due to the transformation of Fe_3O_4 to Fe_2O_3 during the process of firing [21]. Furthermore, the strong intensity peaks 464-474 cm^{-1} are analogous to Si-O-Si bending of silicates of the pottery artifacts.

Table 2 Infrared absorption frequencies (cm^{-1}) with relative intensities of Vadamangalam pot shards and tentative vibrational assignments

IR absorption band (wave number cm^{-1})					Vibrational assignments
VDMP1	VDMP2	VDMP3	VDMP4	VDMP5	
3446VS	3442VS	3440VS	3439S	3443VS	O-H str. of adsorbed water
1636M	1635M	1636M	1631M	1635S	H-O-H bending of adsorbed water
-	-	-	-	1014VS	Si-O str. of kaolinite
1037VS	1033VS	1033VS	1037VS	-	Si-O str. of clay minerals
776M	777S	778M	777S	778S	Si-O symmetrical str. of quartz
692W	692W	692VW	692M	691W	Si-O symmetrical str. of quartz
645W	644W	645VW	-	647VW	Al-O-Si str. of feldspar
578M	581M	-	-	-	Fe-O bend of magnetite
535S	534M	535S	534S	532VS	Fe-O bend of hematite
-	-	-	-	474VS	Si-O-Si bending of silicates
466S	464S	469S	469S	-	Si-O-Si bending of silicates

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

Pondur (12° 56”, 79° 55”) site

The burial urn sample was excavated at Pondur, named as PDR, which is the neck part of the urn. The urn burial seems to be that the black core is sandwiched, which is shown in Fig.2. The FT-IR analyses made for the both red (PDRR) and black (PDRB) parts individually.

In the present work the IR bands were recorded for the Pondur samples given in Table.3. The IR vibrational bands at around 3440 and 1640 cm^{-1} is represent O-H stretching and H-O-H bending of water molecules [22]. For the Pondur samples the very strong broad band around 3432 and 3450 cm^{-1} attributed to the O-H stretching and the medium intensity band around 1634cm^{-1} is to H-O-H bending vibrations of adsorbed water.

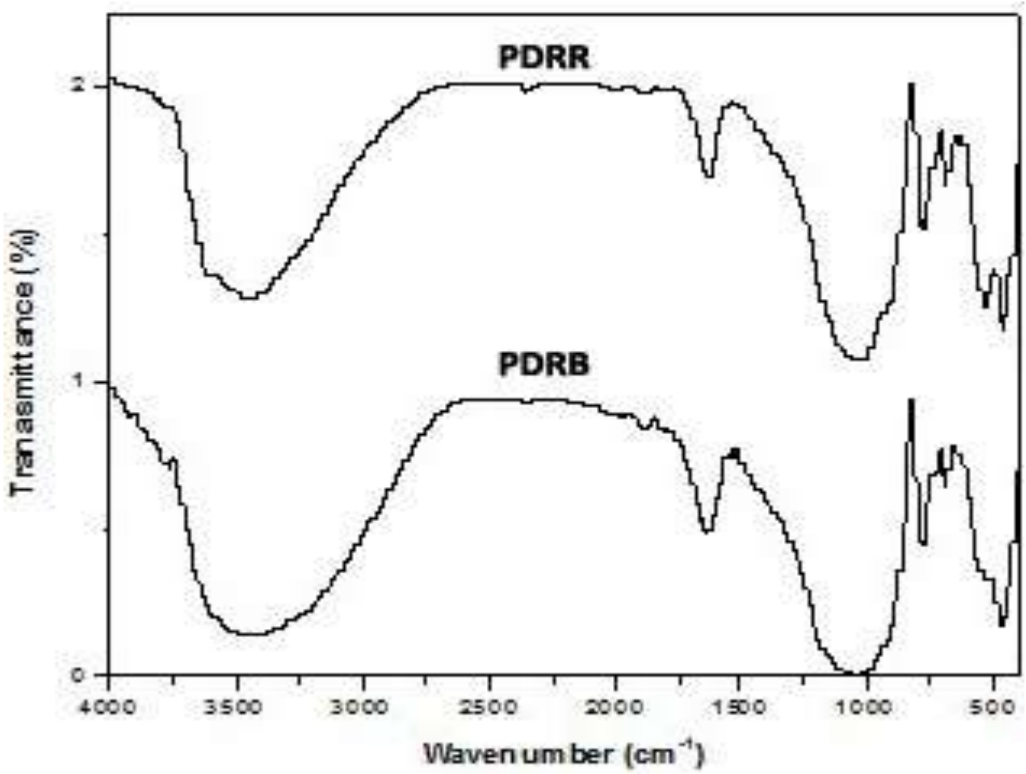

Figure 4 FT-IR spectra of Pondur urn shard (PDRB & PDRR)

Table 3 Infrared absorption frequencies (cm^{-1}) with relative intensities of Pondur pot shards and tentative vibrational assignments

IR absorption band (wave number cm^{-1})		**Vibrational assignments**
PDRR	**PDRB**	
3450 VS	3432 VS	O-H str. of adsorbed water
1633 M	1634 M	H-O-H bending of adsorbed water
1035 VS	1042 VS	Si-O str. of clay minerals
794 M	-	Si-O symmetrical str. of quartz
778 M	778 M	Si-O symmetrical str. of quartz
692 M	691 W	Si-O symmetrical str. of quartz
538 VS	-	Fe-O bend of hematite
470 VS	470 VS	Si-O-Si bending of silicates

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

According to Farmer (1974) and De Benedetto et al (2002), the very strong intensity band at around 1035 and 1042 cm^{-1} is due to the Si–O stretching mode [23, 24]. The band around 1035 cm^{-1} is dehydroxylates and transforms to metakaolinite at about 450–650°C [6, 7].The presence of Si-O stretching band and the absence of Al (OH) stretching of octahedral sheet structure at 915 cm^{-1} are reported that the firing temperature may be 500-650°C. The doublet peak at 794 and 778 cm^{-1} along with 691 cm^{-1} are the attributed to Si-O stretching of quartz [11].

Colour analysis of artifact

The presence of iron, either in pure state or in the form of oxides is the key factor to understand the colour of the artifacts. The colour of the relics is due to the content of iron oxide which acts as the colouring agent. According to Yariv and Mendelovici [25], Mirti et al. [26, 27], and Piero Mirti and Patrizia Davit [28] observed that the colour of the shard is due to hematite which is a red brown solid and decides the atmospheric conditions (oxidizing/reducing) where the artifacts were fired. The burial urn collected from Pondur is named as PDR were in reddish outer layer, that the ceramic material was fired in an oxygen environment [29] (open environment), at least during part of its fabrication. The inner layer of the urn has a dark gray colour. This dark region, called "black core", is associated with there is no attendance of iron oxides in clay [30], whereas the red part of the urn shows that the hematite and PDR probably fired in the reducing atmosphere. The thicker the piece, the more likely the formation of black core and the greater the temperature difference between the surface and the center of the piece in firing [30]. The temperature difference and the firing techniques will be given in future research. The black colour of the urn may be due to the hay. In the early days the very thick part of artifacts were made with the sandwich of hay, it is due to the core part of artifact might not be fired properly. The black part of the urn is not seems to be clay soil, it similar to the hay. From the above discussion, the 2nd centuries AD to 3rd centuries BC period artisans had the knowledge to bake the artifacts in different way. This is the evidence of enhancement of clay technology.

Conclusion

The infrared spectra of the both Vadamangalam and Pondur samples were recorded in the mid infrared region. Quartz, feldspar, kaolinite and iron oxides were present in Vadamangalam samples. Similarly, the quartz, kaolinite and hematite were observed in Pondur sample, but in the case of PDRB vibrational analysis, hematite is absent. In the Pondur sample, the hay was sandwiched in core of burial urn, because the thick part may not fire properly. While using the hay, the whole part of urn is able to fire well. Also all the samples were fired between 500-650°C in the corresponding oxidation/ reduction atmosphere.

This work represents the beginning of a long-term project with the aim of carrying out provenance studies based on the archaeomagnetic studies, which will provide new interesting and useful information about trade routes and production technologies.

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References

[1] Rye, O., 1981. *Pottery Technology: Principles and Reconstruction*. Taraxacum Inc., Washington.
[2] Gosselain, O.P., 1992. Bonfire of the enquiries: pottery firing temperatures in archaeology: what for? *Journal of Archaeological Science* 19, 243-259.
[3] H.V. Olphen, J.J. Fripiat (Eds.), *Data Handbook for Clay Materials and other Non-Metallic Minerals*, Pergomon Press, New York, 1979.
[4] G. Parthasarathy, Effect of High-Pressures on the Electrical Resistivity of Natural Zeolites from the Deccan Trap, Mahrashtra, India, *Journal of Applied Geophysics* Vol. 58, No. 4, pp. 321-329.
[5] G. Parthasarathy, A. C. Kunwar and R. Srinivasan, Occurrence of Moganite-Rich Chalcedony in Deccan Flood Basalts, Killari, Maharashtra, India, *European Journal of Mineral*, Vol. 13, No. 1, 2001, pp. 127-134.

[6] E. Mendelovici, *J. Therm. Anal*. 49 (1997) 1385.
[7] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, *Appl. Clay Sci*. 20 (2001) 73.
[8] Elsass, F., Oliver, D., 1978. Infrared and electron spin resonance studies of clays representative of the sedimentary evolution of the basin of Autun. *Clay Minerals* 13, 299.
[9] V. Ramasamy, G. Suresh, *American-Eurasian Journal of ScientificResearch*, 4 (2009) 103-107.
[10] K. Janaki, G. Velraj, *Recent Research in Science and Technology*, 3 (2011) 89-91.
[11] Russell J D, *A hand book of determinative methods in clay mineralogy*, (ed. Wilson, M.J., Blackie and Son Ltd), 1987.
[12] S.H. Yariv, E. Mendelovici, *Appl. Spectrosc*. 33 (4) (1979) 410.
[13] H. Kodama, *Infrared spectra of minerals, reference guide to identification and characterization of minerals for study of soils*, Tech, Bull, 1985-IE, Research branch, Agriculture, Canada, 1985.
[14] D. Barilaro, G. Barone, V. Crupi, M.G. Donato, D. Majolino, G. Messina, R. Ponterio, *J. Mol. Struct*. 744–747 (2005) 827–831.
[15] W. Griffith, in: R.J.H. Clark, R.E. Hester (Eds.), *Advances in the Raman and Infrared Spectroscopy of Inorganic Based Materials*, Wiley, Chichester, 1987, Chapter 2.
[16] P. Mirti, A. Perardi, M. Gulmini, *Archaeometry* 48 (1) (2006) 31–43.
[17] Piero Mirti, Patrizia Davit, *J. Archaeol. Sci*. 31 (2004) 741–751.
[18] S. Akyuz, T. Akyuz, S. Basaran, C. Bolacal, A. Gulec, *J. Mol. Struct*. 834–836 (2007) 150– 153.
[19] A. Livingstone Smith, *J. Archaeol. Sci*. 28 (2001) 991–1003.
[20] O.P. Gosselain, *J. Archaeol. Sci*. 19 (1992) 243–259.
[21] G.O. Harrell, R.R. Russell, *Influence of Ambient Atmosphere in Maturation of structural products*, Bulletin 204, Engineering Experiment station, Chio state University, Columbus, 1967.
[22] M.A. Legodi, D. de Waal, *Spectrochimica Acta Part A*, 66 (2007) 135-142.
[23] Farmer, V.C., 1974. *Infrared Spectra of Minerals*, Ed. Mineralogical Society, London.
[24] De Benedetto, G.E., Laviano, R., Sabbatini, L., Zambonin, G.P., 2002. Infrared spectroscopy in the mineralogical characterization of ancient pottery. *Journal of Cultural Heritage* 3, 177– 186.
[25] S.H. Yariv, E. Mendelovici, *Appl. Spectrosc*. 33 (4) (1979) 410.
[26] P. Mirti, A. Perardi, M. Gulmini, *Archaeometry* 48 (1) (2006) 31–43.
[27] P. Mirti, M. Gulmini, A. Perardi, P. Davit, D. Elia, *Anal. Bioanal. Chem*. 380 (2004) 712–718.
[28] Piero Mirti, Patrizia Davit, *J. Archaeol. Sci*. 31 (2004) 741–751.
[29] M.R.Rice, *Pottery Analysis: A Sourcebook*, University of Chicago Press, Chicago, 2005.
[30] P.V.Kirch, Int. Encycl. Soc. *Behav. Sci*. (2004) 1623-1627.

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