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PHYSICS

SPECTROSCOPIC AND MICROSCOPIC STUDIES OF ARCHAEOLOGICAL CELADONS RECENTLY EXCAVETED FROM ALAGANKULAM, TAMILNADU, INDIA

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Abstract
Ceramics are the most common archaeological material used by the historians to draw chronological and cultural characterizations. Among these, porcelains and celadons are recognized as good historical relics. Moreover, the different facets of science, technology and culture are also imprinted in these samples. Hence, the knowledge of microstructures, compositions and technologies used can be helpful in identifying and dating the ancient artifacts. In this paper, three representative celadon samples found in the course of archaeological excavations at the site Alagankulam, Ramanathapuram District, Tamilnadu, India were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) in order to achieve their mineralogy and chemical behavior. X-ray diffraction was used to accomplish possible crystalline mineral phases within the clays that composed of samples. On the other hand, FT-IR studies helped in identifying the different mineral assemblages from the tentative vibrational assignments of absorption bands. Microstructure and one or multi step firings can be inferred from the SEM.

Keywords: XRD, FTIR, SEM, Archaeological celadons, Mineralogy, Firing technology

Introduction
Ceramic products are highly complicated multi component heterogeneous systems. This means that many different phases including the crystalline and glassy can be distributed in a specific manner. In ceramic production, the same starting material could give different kinds of products if different technologies were applied or the same technology applied to different materials could give different products also (Seung Wook Ham et al., 2002 and Liem et al., 2002). Some of the world's most coveted and admired master pieces of ceramics are porcelain and celadon. They were the result of highly sophisticated technology and can be identified according to their outward appearance (Le et al., 1995).

A detailed examination of ceramics could give valuable information on the characterization and identification of archaeological items. It could also provide the knowledge about the processing used and its time evaluation (Nguyen Quang Liem et al., 2000). However, the identification is not easy because of their similar appearance. This is especially serious if one intentionally makes imitations of rare and precious items (Kingery, 1984 and Vandiver, 1990). Therefore, quantitative techniques are needed to examine compositions and microstructure so that we can characterize the ceramic items and related technology.

FTIR spectroscopy is frequently used method to investigate the structure, bonding and chemical properties of clay minerals (Madejova, 2003) often in combination with XRD and SEM. Usually clay is a mixture of minerals, which can be identified by using the XRD technique. From the micro structural point of view, SEM enables to obtain information about the processing which was used. For the present investigation, representative archaeological inlaid celadon sherds (AGMC-1, AGMC-2 and AGMC-3) belonging to 500 BCE to 1200 CE, excavated from Alagankulam, Ramanathapuram District, Tamilnadu, India were analyzed by XRD, FTIR and SEM.

Experimental Details
The characterization of celadon is carried out with a number of experimental approaches in order to investigate all the relevant features. The samples used in this study were in shred shape. Depending on the technique, the samples were prepared in different forms. For X-ray diffraction and FTIR measurements, the samples were powdered. However, to get better micrograph of the microstructures, the samples were prepared in the form of cross-cut pieces (cutting in the

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glaze/body/glaze direction) of cross-cut pieces in the order of millimeter each. The samples studied are shown in Fig. 1.

The FTIR spectra were recorded in the mid IR frequency region 4000 - 400 cm^{-1}, using Perkin-Elmer spectrometer by KBr pellet technique. The accuracy of the measurement is about ±4 cm^{-1}. X-ray diffraction data were obtained using a XPERT-PRO diffractometer equipped with CuK_α radiation source at a wavelength of 1.5405 Å. The spectra were recorded in the two-theta (2θ) range from 20 to 80^0. Morphology of the sherds determined by NITMME S-3000H Scanning Electron Microscope and the images were obtained with a secondary electron detector.

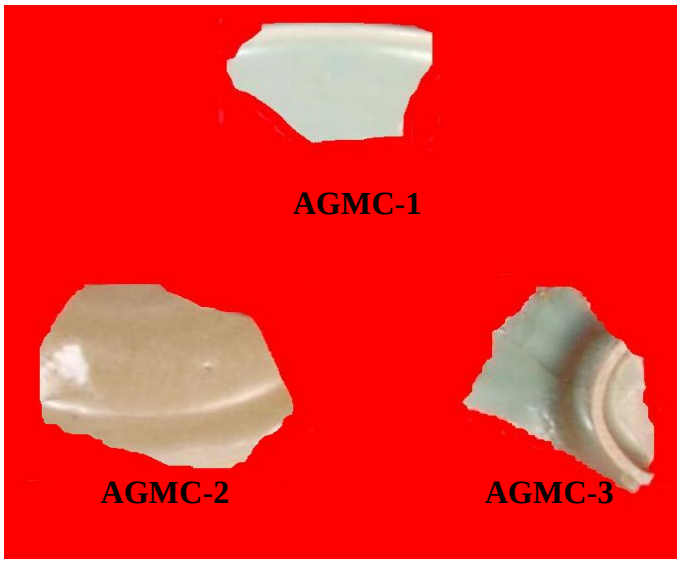

Fig. 1. Celadon sherds of Alagankulam site

Results and Discussion

FTIR characterization

FTIR studies help in the identification of various forms of the minerals present in the celadon. The coupled vibrations are appreciable due to the availability of various constituents. Nevertheless, observed bands (in the range 4000-400 cm^{-1}) have been tentatively assigned. Typical IR spectra of all samples recorded are shown in Fig. 2 and their tentative vibrational assignments with relative intensities are presented in Table 1.

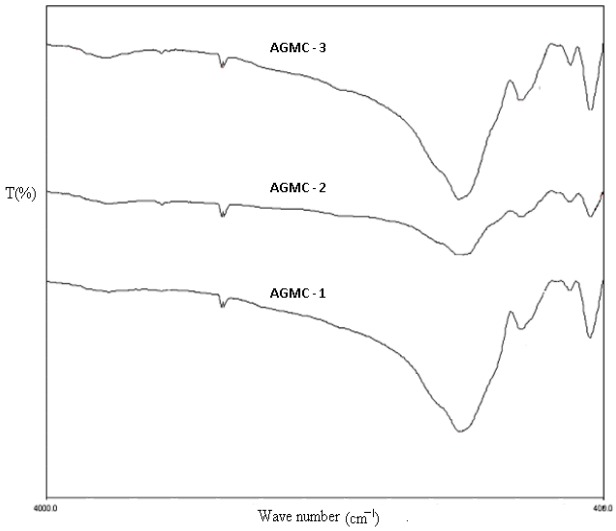

Fig.2 FT-IR spectra of Alagankulam celadon sherds in the as-received state

Table 1. FTIR vibrational assignments of the observed frequencies of Alagankulam celadon sherds

Celadon Samples			Tentative vibrational assignments
AGMC-1	AGMC-2	AGMC-3	
Frequency with relative intensity (cm^{-1})	Frequency with relative intensity (cm^{-1})	Frequency with relative intensity (cm^{-1})	
-	-	3690 VW	O-H str. of kaolinite
-	3448 VW	3448 VW	O-H str. of adsorbed water
3421 VW	-	-	O-H str. of adsorbed water
2927 VW	2923 VW	2927 VW	C-H str. of organic matter
2852 VW	2853 VW	2857VW	C-H str. of organic matter
1078 M	1078 M	1078 M	Si-O str. of clay minerals
-	794 VW	795 VW	Si-O symmetric str. of quartz
780 VW	779 VW	779 VW	Si-O stmmetric str. of quartz
670 VW	-	670 VW	Si-O of quartz
558 VW	556 VW	555 VW	Al-O str. of mullite
464 VW	465 VW	467 VW	Si-O orthoclase
-	-	463 VW	Microcline
-	-	457 VW	Illite
-	405 VW	-	Gehlenite

M-medium, VW-very weak

From the FT-IR spectra, it is clear that the very weak band at 3690cm^{-1} in AGMC-3 indicates the presence of O-H stretching of Kaolinite (Krishna bukka et al., 1992). A broad absorption band at 3448 cm^{-1} in AGMC-2 and AGMC-3 and very weak band at 3421cm^{-1} in AGMC-1 are due to O-H stretching of adsorbed water (Neal et al., 1977 and Legodi et al., 2007). Lara Maritan et al and Colombini et al have reported that the two weak peaks observed at 2852cm^{-1} and 2922 cm^{-1} are due to C-H stretching mode and reveal the presence of some organic contribution (Colombini et al., 2005 and Lara Maritan., 2005). Thus, in the present study, a very weak band in the region 2923-2927cm^{-1} and 2852-2857cm^{-1} in all the samples can be assigned to C-H stretching of organic matter.

The broad symmetry band around 1078 cm^{-1} with medium intensity in all the shreds reveals the presence of silicates (Si-O) structure and also show the evidence of white clay type out of which the body of inlay celadon have been made (Gosh, 1978). A very weak doublet at 795 and 779 cm^{-1} in the sample AGMC-2 and AGMC-3 is attributed to quartz. Whereas the sample AGMC-1 validate the Si-O quartz band at 780 cm^{-1} (Russell, 1987). The sample AGMC-1 and AGMC-3 which show the absorption band positioned around 670 cm^{-1} may also be assigned to Si-O mode of quartz (Palanivel et al., 2007). From this study we infer that quartz is invariably present in all samples.

At high firing temperature the kaolinite clay converted to metakaolinite and then to γ-Al_2O_3 and finally to mullite (Brown et al., 1985, Mackenzie et al., 1985 and Meinhold et al., 1985). According to Hartmut Schneider et al the band around 548 – 578 cm^{-1} is assigned to octahedral Al-O stretch of mullite (Hartmut Schneider et al., 2005). Thus, in the present study very weak band at 558 cm^{-1}, 556 cm^{-1} and 555 cm^{-1} in AGMC-1, AGMC-2 and AGMC-3 respectively shows the Al-O stretch of mullite. The presence of mullite in the sherds is also an evident of high firing temperature.

The presence of very weak bands around 464 cm^{-1} and 465 cm^{-1} in AGMC-1 and AGMC-2 respectively refers the orthoclase (Omori, 1974) whereas the band at 463 cm^{-1} in AGMC-3 shows the microcline (Farmer, 1967). The sample AGMC-3 indicate the possibility of illite as referred by the band at 457 cm^{-1} (Preethi Sagar Nayak et al., 2007 and Kieffer, 1979) and AGMC-2 confirms the presence of gehlenite by a very weak band at 405 cm^{-1} (Kimata, 1980 and Dowty, 1987).

XRD characterization

XRD is used to determine the mineralogical composition as well as qualitative and quantitative phase analysis of multiphase mixtures. XRD measurements are supportive to the information obtained with IR spectroscopy. In Fig. 3 the diffraction patterns of the shards AGMC-1, AGMC-2 and AGMC-3 are presented. The presence of major minerals is identified by comparing 2θ values with the JCPDS (Joint Committee on Powder Diffraction Standards) file (JCPDS 2003).

The peaks of the main components are indicated as quartz (Q), mullite (M) and traces of orthoclase (K-feldspar), plagioclase feldspar, microcline, illite and Gehlenite. The small percentage of mullite present is supportive of the fact that the sherds originate from southern China. All of these minerals are typical of Chinese raw materials and support the Chinese origin of the celadon (Linda et al., 2005).

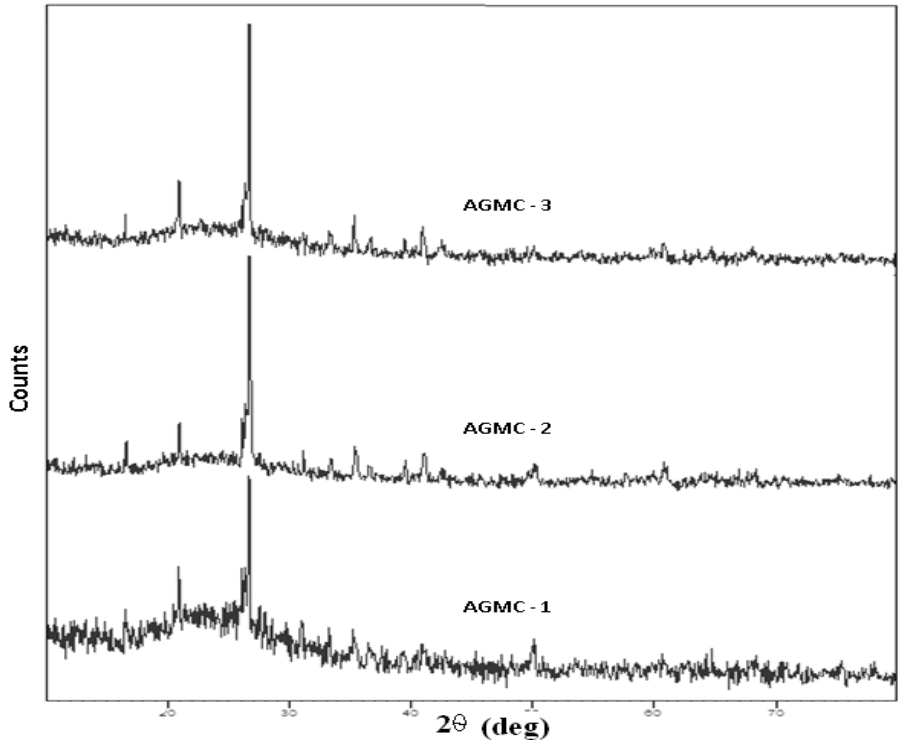

Fig.3 X- ray diffraction pattern of Alagankulam celadon sherds

Scanning Electron microscopy

Morphologies, as observed by scanning electron microscopy (SEM), can also be useful in identification of minerals and firing technology. From the images of with medium magnification, one can see the body, the transitional region and the glaze, in which the technological features are imprinted since the production. These are especially good for the interpretation of firing procedure namely one- or multi-steps (Nguyen Quang Liem et al., 2000 and Liem et al., 2002).

Fig.3 presents the micrographs of celadon sherds. There is a gradual change in microstructure from the body to the glaze which recognizes the one step technology (Fig. 3a). Relatively large and also tiny bubbles occur in the glaze. The glaze is much vitrified than the bodies due to the higher content of flux. The higher magnification makes the identification of the minerals possible

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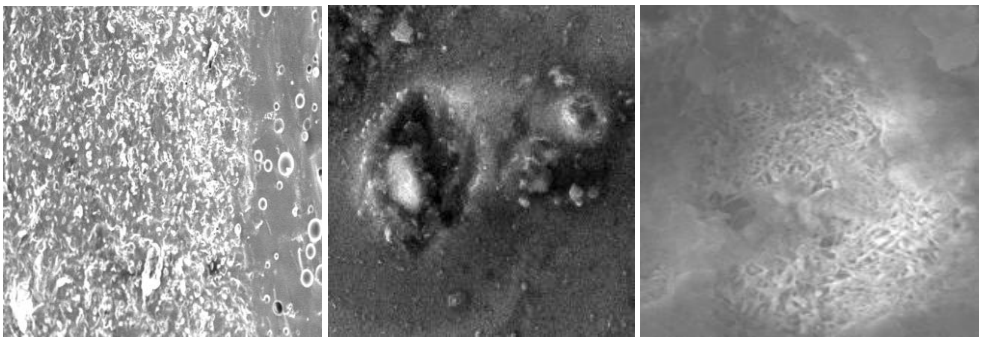

(a) (b) (c)

Fig.3. SEM microphotograph of inlaid celadon

Many grains did not dissolve completely in the body but evolved from the outermost to transform into other phases (Fig.3b). Some others almost dissolved, which gives rise to mullite micro-crystallites. With SEM technique, we observed needle shaped mullite at the body/glaze interface region (Fig.3c) (Kingery, 1960).

Conclusion

By the application of the techniques of IR spectroscopy, X-ray diffraction and scanning electron microscopy, it was possible that to determine the mineralogical composition and firing steps of three samples of celadon sherds from Alagankulam. XRD study shows the presence of quartz, mullite and a mineral from feldspar group (orthoclase and microcline). Other phases of less impotance which are also present are illite and Gehlenite. The presence of above minerals was further confirmed by FTIR using tentative vibrational assignments. These types minerals are not possible at this archaeological site and these celadon sherds may be transport from china. From SEM it is evident that a one-step or multi-step firing technique which is not aware of our artisans at this time and thus it is manufactured from china. By this way it is well evident that there might have been a trade link between India and china through this archaeological site.

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