Available at www.ijsred.com

RESEARCH ARTICLE OPEN ACCESS

# Magnetic, Mossbauer and Micro-Analytical Findings of Archaeological Pottery Sample of Manaveli, India

G. Raja Annamalai[a*], R. Ravisankar[b], A. Chandrasekaran[c]

[a]Department of Physics, Valliammai Women's College of Arts & Science, Arakandanallur- 605752, Villupuram, Tamilnadu, India.
[b]Post Graduate and Research Department of Physics, Government Arts College, Tiruvanamalai-606 603, Tamilnadu, India.
[c]Department of Physics, SSN College of Engineering, Kalavakkam, Chennai - 603110, Tamilnadu, India.

----------------------------------------************************----------------------------

**Abstract**

The magnetic properties of archaeological pottery specimen combined with Mössbauer study can provide useful results for their characterization. The main objectives of the present investigation are to determine the technological factors applied for the pottery manufacturing (temperature, heating conditions, and duration of heating of the pottery). In order to do these findings, the pottery clay samples collected from the archaeological site Manaveli, Puducherry, India are analyzed. Different analytical methods such as Mössbauer, scanning electron microscopy coupled with energy dispersive spectrometer and vibrating sample magnetometer have been utilized to evaluate the firing temperature and firing conditions of the samples during their production.

**Keywords:** Archaeological pottery sample, Mössbauer study, Micro structural and chemical analysis, vibrating sample magnetometric study.

----------------------------------------************************----------------------------

## 1. Introduction

The ancient pottery plays an important role of information regarding the civilizations which have produced and used it. The analysis of ancient archaeological pottery assists to know the cultural heritage of ancient people, technological skills and trade patterns of ancient civilization. The several methods have estimated the firing temperature of the ancient pottery samples. Amongst one method has been employed, such as the study of sintering and vitrification of the clay matrix by observing the microstructure by scanning electron microscopy (SEM) [1]. Mössbauer study provides a prominent potential in the analysis of the chemical and physical changes appearing in pottery clays during its firing [2]. The change in magnetic properties of the pottery shards also determines the technology of pottery production studied by vibrating sample magnetometry (VSM) [3].

In the present work, the pottery samples collected from the archaeological site Manaveli, Puducherry, India were characterized by different methods like SEM coupled with EDX, Mössbauer and vibrating sample magnetometry (VSM) have been employed to estimate the firing temperature and firing atmosphere.

  

## 2. Experiment

### *2.1. Samples*

Manaveli is one of the archaeological sites in Puducherry Union Territory, India. The pottery sample was excavated from Manaveli (11˚53′26″N; 79˚48′32″E), by the Department of History, University of Pondicherry, Puducherry, India. The pottery shred of Manaveli belongs to the Iron Age grave century ($5^{th}$ century BC). Red ware was collected on this site. The visual photograph of the collected pottery sample is shown in Fig-1. The sample is designated as MP. The layer of clay deposited on the surface of the pottery sample at a depth of 30 cm during excavation was removed, and the pottery shred was grounded into the fine powder using agate mortar.

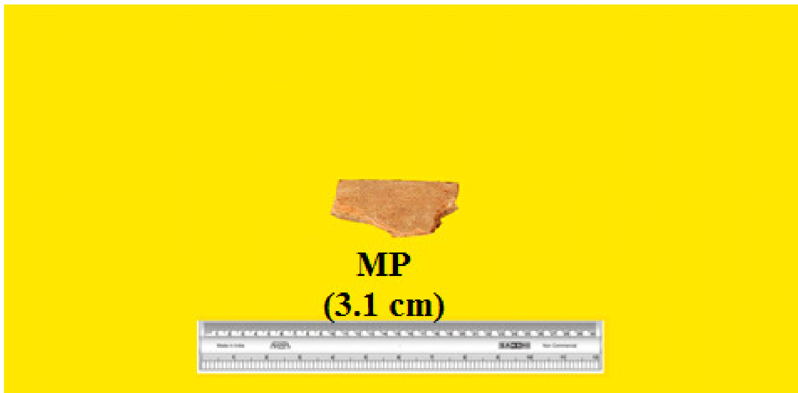


**Fig. 1. The visual photograph of the Red ware pottery sample.**

### *2.2. Methods*

*Micro structural and chemical Techniques (SEM-EDS):* The microstructure of the archaeological pottery sample was studied by using SEM Quanta FEI, Netherland. The maximum magnification possible in the equipment are 3,00,000 times with an accurate resolution of 3nm. The elemental identification of the sample was carried by using the Oxford INCA Energy Dispersive Spectrometer (EDS). The powdered pottery sample coated with a thin layer of platinum was employed using SEM, typically set at a magnification of X 2000 times of the study.

*Mössbauer study*: The Mössbauer measurements have been carried out with a conventional constant acceleration spectrometer (M /s WISSEL, Germany) equipped with a room temperature Rh matrix 57Co source. The hyperfine parameter isomer shift (IS), quadrupole splitting (QS), the full line width at half maximum (W), expressed in mm /s, and the internal magnetic field Hint, expressed in Tesla, have been obtained by means of a standard least-squares minimization technique. The spectrum is fitted to Lorentzian line shapes using a minimum number of doublets and sextets. The spectrum recorded at room temperature is fitted to a PC with a least squares minimization procedure assuming Lorentzian line shapes.

*Magnetic measurements:* Magnetization curves of the powdered pottery and clay fragments were made with a vibrating sample magnetometer (Princeton Measurements Co. MicroMag VSM & AGM 2900-3900). The maximum field applied was 13 kOe.

  

## 3. Results and Discussions

### *3.1. Micro structural and chemical Analysis*

The microstructure of the clay and pottery matrix with the help of Scanning Electron Micrograph has been investigated (Fig. 2 & 3). The maximum temperature reached during the pottery firing process and the association with various vitrification stages was studied by many authors such as Maniatis and Tite [4], and Tite et al [5].

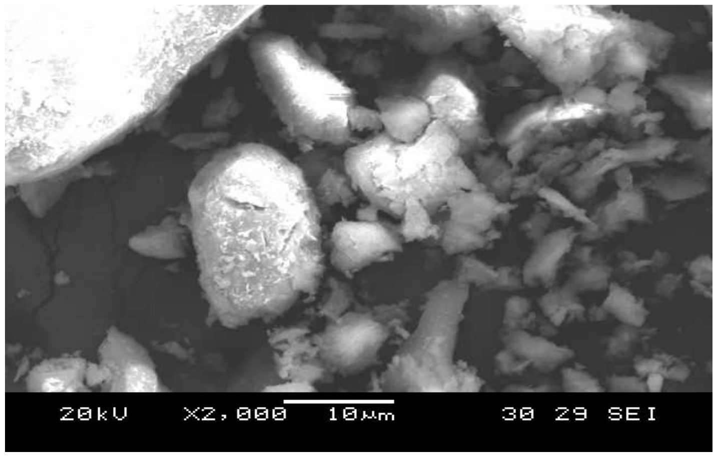


**Fig. 2. The image of Scanning Electron Micrograph for 'as received state pottery sample.**

In order to get exact results of firing temperature of the archaeological pottery, the sample was refired to a temperature at 850°C in the muffle furnace and SEM image of the sample recorded. The SEM image of the refired sample was compared with the image of 'as received state sample.

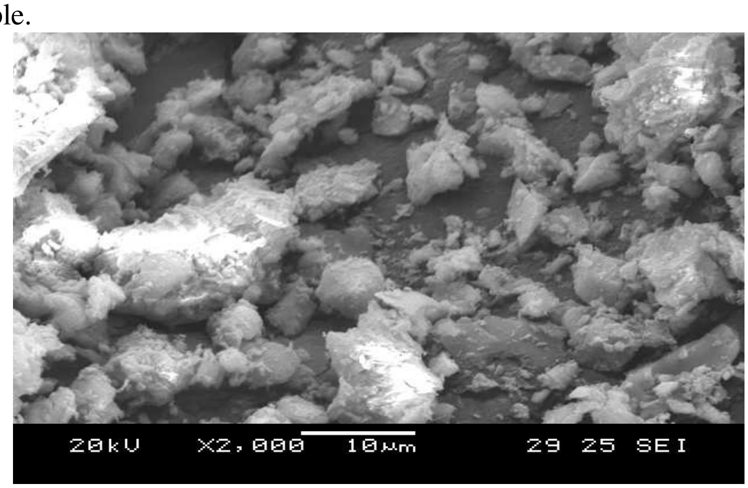


**Fig. 3. The image of Scanning Electron Micrograph for refired pottery clay sample.**

From the studied SEM image of the clay sample fired at 850°C shows similar characteristics with the 'as received state pottery sample. The image of Scanning Electron Micrograph for 'as received state pottery sample (Fig. 2) shows different grain sizes with irregular shaped and some slight rounding of the edges of the pottery. This structure of different grain size with slight rounding edges is found as intermediate between the initial vitrification and no-vitrification stages [4]. The image of Scanning Electron Micrograph for refired pottery clay sample (Fig. 3) has more rounded edges which are an evidence of the initial vitrification stage [6]. Yariv and Mendelovici [7] have investigated that the vitrification stage of the sample was initial vitrification stage that the pottery might have been heated in the temperature range 800-850°C in the oxidizing condition during at the time of manufacturing.

From the above discussion, one can conclude that the sample had been fired at a temperature of around 800°C in the oxidizing atmosphere during pottery production.

The energy dispersive X-ray spectrum of the received state sample is shown in Fig. 4. The EDS analysis of the sample reveals that the existences of the varied percentage of the elements such as silicon, aluminum, potassium, iron, magnesium and sodium as the predominant constituents in the pottery. If the pottery specimen contains less than 6% of calcium content, the clay used for making the pottery is of the non-calcareous type of clay [4]. Based on the information collected from EDS analysis it is revealed that the elemental characterization by EDS analysis shows that the pottery is non-calcareous clay type since the percentage of Ca observed in this sample is 3.04%.

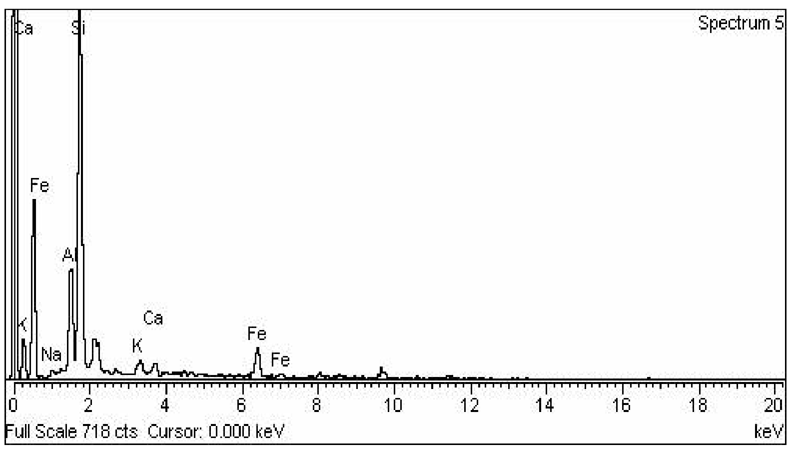


**Fig. 4. The Energy Dispersive X-ray spectrum of the received state sample.**

Maniatis and Tite stated that, if the fluxes concentration ($K_2O$, $Fe_2O_3$, CaO, MgO, and $TiO_2$) are more than 9% the lays are classified as low refractory and classified as high refractory if the fluxes in the sample are less than 9% clays [4]. The energy dispersive spectrum clearly inferred that the sample is low refractory in nature and the sample had high iron contents.

From the above discussion, one can conclude that the sample had been fired at a temperature of around 800°C in the oxidizing atmosphere during pottery production.

### *3.2. Mössbauer study*

Fig. 5 shows Mössbauer spectrum of Manaveli pottery sample. The Mössbauer parameters such as isomer shift, quadrupole splitting, and magnetic hyperfine interaction have been derived from the peak position of the spectrum. The study of Mössbauer spectra on archaeological pottery was carried out in detail by many authors [8-10] in order to find the presence of magnetic components, and their transformation due to heating, heating atmospheres, and coloring mechanism.

  

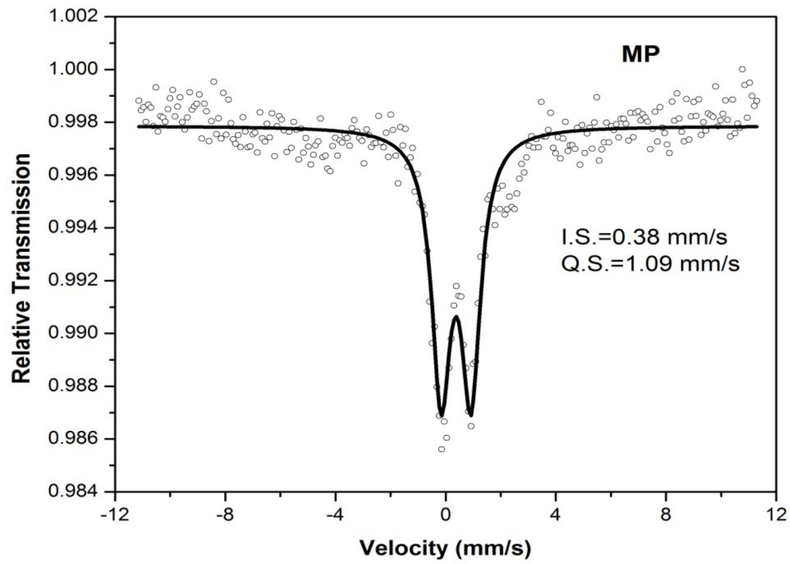


**Fig. 5. Mössbauer spectrum of the Manaveli pottery sample.**

The presence or absence of paramagnetic $Fe^{2+}$ and $Fe^{3+}$ ion from the peak position of Mössbauer spectrum have analyzed the firing condition, firing temperature and coloring mechanisms of the archaeological potteries. The decrease or disappearance of $Fe^{2+}$ ion reveals that oxygen is rich in original firing condition due to the firing of the sample in the oxidizing atmosphere. The pottery had been fired under oxidizing atmosphere; at temperatures greater than 500°C shows no $Fe^{2+}$ in its Mössbauer spectrum. Coey [11] reported that the value of the isomer shift (δ) ranging from 0.8 to 1.5 mm/s and the value of quadrupole splitting (Δ) from 1 to 3.5 mm/s are identified to $Fe^{2+}$, the isomer shift value from 0.2 to 0.6 mm/s and quadrupole splitting value from 0 to 1.8 mm/s are indicated to $Fe^{3+}$.

The Mössbauer spectrum of the Manaveli pottery sample shows the presence of paramagnetic $Fe^{3+}$ and iron oxide, namely, hematite because the value of isomer shift 0.38 and quadrupole splitting value of $Fe^{3+}$ (1.09 mm/s) were identified in the sample. The absence of $Fe^{2+}$ reveals that the specimen has been fired in a strong oxidizing atmosphere. The high percentage of non-magnetic $Fe^{3+}$ and the presence of poor crystalline mineral of iron oxide, namely, hematite in the spectrum infer that the archaeological pottery sample was not fired at a temperature greater than 900°C.

From aforesaid reason, it was concluded that the specimen was fired under oxidizing condition; the same is also an indication of the reddish-brown color of the outer surface. The reddish-brown color is due to the presence of hematite. The observed value of isomer shift 0.38 and quadrupole splitting value of $Fe^{3+}$ (1.09 mm/s) confirms the firing temperature of this sample as around 800°C in the oxidizing atmosphere during pottery production, which is in good agreement with the SEM-EDS analysis [12].

### *3.3. Magnetic Characterization*

Magnetic hysteresis loop for Manaveli pottery in 'as received state sample is shown in Fig.6. It may be noted that the saturation (Ms) and the remanent magnetic specific moments of the investigated Manaveli pottery sample. The analysis of the hysteresis curve shape is very useful for the estimation of the magnetic behavior of the pottery sample. According to

  

Beatrice et al. (2008), the sample of Manaveli exhibit low coercivity behavior studied by nearly-reversible magnetization curve and low $M_R/M_S$=0.32 [13]. These features are associated with a relevant content of superparamagnetic iron oxide particles.

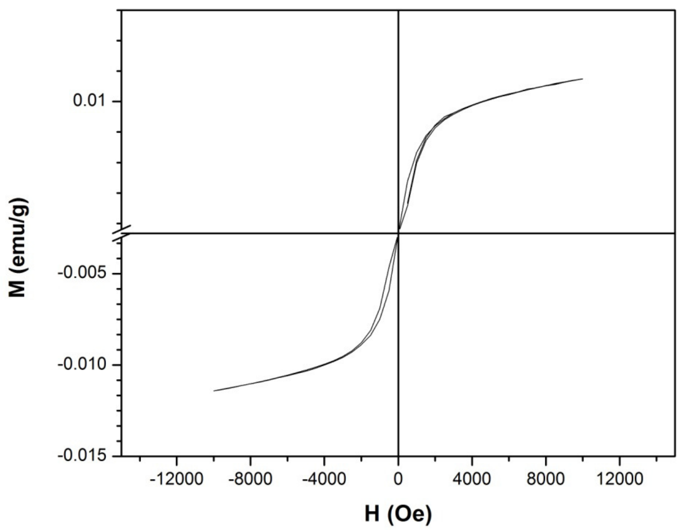


**Fig. 6. Magnetic hysteresis loop for Manaveli pottery in 'as received state sample.**

The remanent magnetization of pottery clay sample is dominated by iron phases such as magnetite and hematite. These Fe ions are not in contact with each other and cannot provide Ferri- or anti-ferromagnetic properties, their only contribution is in paramagnetic nature. The magnetic and color features of common pottery are due to iron oxides already evidenced by Mössbauer analysis. Van Klinken (2001) pointed out firing processes at a temperature above 750°C redistribute the fraction of silicate-bound Fe into ''free'' iron oxides [14]. The results of magnetic study give well-supporting information obtained from the SEM-EDS and Mössbauer analysis.

## 4. Conclusion

This work infers the systematic use of three physical methods of study such as SEM coupled with EDS, Mössbauer, and VSM on one pottery sample. All these analyses revealed that pottery of Manaveli was fired in the temperature range 750-800°C and which indicate the presence of iron oxide mineral hematite had been formed during manufacturing due to heating (phase transformation). Finally, these analytical studies which confirm this sample were fired at a temperature greater than 750°C in the oxidizing condition at the time of pottery production.

## References

[1] Maniatis, Y., Tite, M. S. (1975). A scanning electron microscope examination of the bloating of fired clays. *Transactions and Journal of the British Ceramic Society*. 74: 229-232.

[2] Wagner, F.E., Wagner, U. (2004). Mössbauer Spectra of Clays and Ceramics. *Hyperfine Interactions.* 154: 35–82.

[3] Cultrone, C., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., de la Torre, M.J. (2001). Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy*. 13(3): 621.

[4] Maniatis, Y., Tite, M.S. (1981).Technological Examination of Neolithic-Bronze Age Pottery from Central and Southeast Europe and from the Near East. *Journal of Archaeological Science.* 8: 59-76.

[5] Tite, M.S., Freestone, I.C., Meeks, N.D., Bimson, M. (1982). The use of scanning electron microscopy in the technological examination of ancient ceramics. In:Franklin, A.D., Olin, J. (Eds.), Ceramics as Archaeological Material. Ceramic as Archaeological Material, pp. 109–120.

[6] Ravisankar, R., Kiruba, S., Shamira, C., Naseerutheen, A., Balaji, P.D., Seran, M. 2011. Spectroscopic techniques applied to the characterization of recently excavated ancient potteries from ThiruverkaduTamilnadu, India**.** *Microchemical Journal*. 99: 370–375.

[7] Yariv, S.H., Mendelovici, E. (1979). The Effect of Degree of Crystallinity on the Infrared Spectrum of Hematite. *Applied Spectroscopy*. 33(4): 410-411.

[8] Shimada, I., Wagner, U. (2001). Peruvian Black Pottery Production and Metalworking: A Middle Sicán CraftWorkshop at Huaca Sialupe. *MRS Bulletin*. 26: 25-30.

[9] Wagner, U. Gebhard, R., Hausler, W., Hutzelmann, T., Riederer, J., Shimada, I., Sosa, J., Wagner, F.E. (1999). Reducing firing of an early pottery making kiln at Batan Grande, Peru: A Mossbauer study. *Hyperfine Interactions*. 122: 163–170.

[10] Wagner, U., Gebhard, R., Murad, E., Grosse, G., Riederer, J., Shimada, I., Wagner, F.E. (1997). Formative ceramics from the Andes and their production: A Mossbauer study. *Hyperfine Interactions.* 110: 165–176.

[11] Coey, J.M.D. (1980). Clay minerals and their transformations studied with nuclear techniques: the contribution of Mössbauer spectroscopy. *Atomic Energy Review*. 18: 73-124.

[12] Wagner, U., Wagner, F. E., Häusler, W., Shimada, I. (2000). The use of Mossbauer spectroscopy in studies of archaeological ceramics, in: D. E. Creagh and D. A. Bradley (eds), Radiation in Art and Archaeometry, Amsterdam. pp. 417.

[13] Beatrice, C., Coïsson, M., Ferrara, E., Olivetti, E.S. (2008). Relevance of magnetic properties for the characterisation of burnt clays and archaeological tiles. *Physics and Chemistry of the Earth.* 33: 458.

[14] Van Klinken, J. (2001). Magnetization of Ancient Ceramics. *Archaeometry*. 43(1): 49-57.