

# Applications of FTIR and $^{57}\text{Fe}$ Mössbauer Techniques in Studies of Recently Excavated Indian Archaeological Pottery

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The Fourier transform infrared absorption spectra and  $^{57}\text{Fe}$  Mössbauer spectra have been recorded at room temperature for the recently excavated archaeological pottery sherds. FTIR spectroscopy is used to estimate the lower limit of firing temperature and firing nature of the pottery sherds, and it is confirmed by the results of the Mössbauer technique results. The results show that the  $^{57}\text{Fe}$  Mössbauer and FTIR spectra of few pottery sherds of Perumalpattu and Theriruvveli are nearly identical, indicating that they may belong to the same origin.  $^{57}\text{Fe}$  Mössbauer spectra of black coloured sherds show the presence of  $\text{Fe}^{2+}$  ions which confirm the relation between the black colour in pottery and the existence of non-magnetic  $\text{FeO}$  compound, resulting from the reducing atmospheric condition during firing. FTIR results of reddish pot sherds show the presence of significant amount of  $\text{Fe}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$ , which confirms again the relationship between the state and form of iron present in the pottery and its colour.

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## 1. Introduction

To preserve the past, one must have not only the objects, but also an understanding of the knowledge and skills used to produce them. The artistic object or archaeological artifacts like painting, stone sculpture, astrolabe, potsherd and ugly fragment of furnace represent specific knowledge, meaning and culture, which inspires museums to study them and preserve for restudy.

Through contextual analysis and deconstruction of artifacts, one can go back to the time of a critical understanding how ancient people used craft and technology to solve problems of survival and organization, and to make symbols or representations of what was important in their world, especially for its maintenance, longevity, and beautification. This process is known as material culture and cultural heritage [1].

The technical and artistic quality of pottery are important indicators, for the achievements of prehistoric societies, which have left no written records, but nevertheless often have highly developed handicrafts [2].

Therefore, this study is about the determination of lower limit of firing temperature, firing atmosphere and translocation of recently excavated archaeological pottery sherds of Perumalpattu and Theriruvveli, Tamilnadu State, India.

## 2. Importance of excavated site location

In India, Tamilnadu State is well known for its cultural heritage and civilization for the past 2000 years. Perumalpattu and Theriruvveli are the locations identified as archaeological sites by the State Department of Archaeology, Government of Tamilnadu, India. The archaeologists have found that the potteries excavated at Perumalpattu and Theriruvveli are almost identical in their symbols, colour and representations. In this work, the archaeological pottery sherds were collected from sites at Perumalpattu [13°07' Lat.N; 80°01' Long.E] and Theriruvveli [9°19' Lat.N; 78°38' Long.E]. Dhanapandian [3] has adopted archaeomagnetic dating technique on the above potteries and reported that pottery sherds collected from Perumalpattu belonged to the 9th century AD, whereas Theriruvveli potteries belonged to the period between the 8th and the 10th century AD. The results of archaeomagnetic dating are similar with the predictions of archaeologists from Tamilnadu. Further, the rouletted type pottery sherds identified from Theriruvveli site indicate that the place has trade links with Rome and other countries during the archaeological period.

## 3. Materials and methods

The pottery sherds collected from the Perumalpattu site are named PMU-1, PMU-2, PMU-3, PMU-4, PMU-5, PMU-6, PMU-7, and PMU-8, and those from Theriruvveli site are TRI-1, TRI-2, TRI-3, TRI-4, TRI-5, TRI-6, TRI-7 and TRI-8.

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### 3.1. FTIR spectroscopy

Different coloured pottery sherds collected from Perumalpattu and Theriruvveli were subjected to refiring at different temperatures such as 300, 500, and 800 °C for one hour in air using laboratory electric furnace and allowed to cool in the furnace to room temperature. Then the samples were hand grinded to a fine particle size of less than 2  $\mu\text{m}$  using agate mortar. The grinding time was maintained uniformly for all the samples. To remove the moisture present in KBr, the required quantity was taken and dried at 150 °C for about 24 h in an oven. The samples were pelleted by mixing with the spectra grade KBr in the ratio of 1:20 by weight [4]. The FTIR absorption spectra were recorded in the range of frequencies 4000–400  $\text{cm}^{-1}$ , using Model 500, Perkin-Elmer spectrophotometer with 16 scan mode. The accuracy of the instrument is  $\pm 4 \text{ cm}^{-1}$  in 4000 to 2000  $\text{cm}^{-1}$  region and  $\pm 2 \text{ cm}^{-1}$  in 2000 to 400  $\text{cm}^{-1}$  region. Each time before recording the spectra of samples the instrument was calibrated using polystyrene film as standard.

### 3.2. $^{57}\text{Fe}$ Mössbauer spectroscopy

$^{57}\text{Fe}$  Mössbauer spectra were recorded at room temperature (RT) in transmission mode with a conventional constant acceleration spectrometer equipped with a  $^{57}\text{Co}$  (Rh) source. Absorbers were prepared from powdered sample with a thickness of  $100 \pm 10 \text{ mg/cm}^2$  using a PMM compression holder. The spectra were computer-fitted to a sum of Lorentzian lines by applying the constraints of equal line width and area for the two peaks of each doublet and equal line width and areas in the ratio 3:2:1:2:3 for the six peaks of sextets. Isomer shifts ( $\delta$ ) were referred to the centroid of the spectrum of  $\alpha\text{-Fe}$  at RT. The relative concentrations of the different Fe species were calculated from the spectral area ratio assuming that the factor (probability of effect) was the same in all the implicated species.

## 4. Results and discussion

### 4.1. FTIR analysis of archaeological pottery sherds

Clay-based materials undergo several changes during drying and firing stages as a result of physical, chemical, and mineralogical modifications. These changes can be monitored by FTIR spectroscopy. In the present work, to estimate the lower limit of firing temperature and firing atmosphere of pottery sherds, refiring methodology has been followed. In this method, no changes in the FTIR spectra are to be expected during laboratory refiring of ancient sherds until the refiring temperature exceeds the original firing temperature. In this manner the maximum original firing temperature can be estimated. Changes in the FTIR spectra also occur when the composition of the atmosphere differs in the original and the laboratory firing, e.g., when sherds originally fired under reducing conditions or refired in an oxidizing atmosphere, or vice versa. Extensive studies of estimation of firing temperature and firing atmosphere have already been performed

[5–7]. To have an understanding of the translocation of the pottery sherds of Perumalpattu and Theriruvveli, local clay samples have been collected and subjected to FTIR technique.

Figure 1 presents the room temperature FTIR absorption spectra of local clay samples collected from Perumalpattu and Theriruvveli, where the bands observed at 3700 and 3620  $\text{cm}^{-1}$  are attributed to the presence of kaolinite in disordered form [8]. The above bands of two different clay samples disappeared during firing in the laboratory at 500 °C. According to Wagner et al. [9, 10], kaolinite dehydroxylates at about 400–450 °C during heating in air.

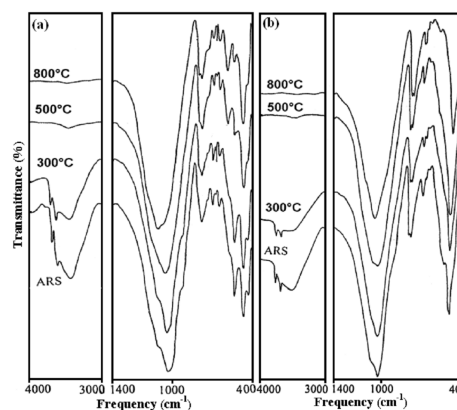


Fig. 1. Room temperature FTIR absorption spectra of clays sample in the as received state (ARS) and as a function of firing temperature. (a) Perumalpattu (PMU), (b) Theriruvveli (TRI).

None of the archaeological pottery sherds of Perumalpattu and Theriruvveli (Figs. 2 and 3 from PMU-1, to PMU-4 and TRI-1 to TRI-4) shows the presence of the bands at 3700 and 3620  $\text{cm}^{-1}$  and it indicates that the sherds have been fired above 450 °C during their manufacture. Wolff [11] studied the kaolinite clays using infrared technique and reported that the bands at 3450 and 1640  $\text{cm}^{-1}$  are attributed to OH stretching and H–O–H bending vibrations of absorbed water molecules which begin to disappear with increasing temperature which means the evaporation of water molecules. The weak shoulder at 915  $\text{cm}^{-1}$  is due to O–H deformation vibrations in the octahedral sheet which begins to disappear with increasing temperature. Wagner et al. [9] and Ghosh [12] have reported that at about 600 °C the expandable layer of silicates collapses, resulting in a broad and strong symmetry band centered at around 1030  $\text{cm}^{-1}$  for red clay or 1080  $\text{cm}^{-1}$  for white clay. None of the representative pottery sherds taken for the present study shows the band at 915  $\text{cm}^{-1}$  implying that all the sherds were fired above 600 °C. Also, the presence of strong symmetry band at around 1030  $\text{cm}^{-1}$  for all sherds confirms that red type clay was used for these potteries.

Russel and Wilson [13] and Ojima [14] have reported that the bands at 795, 775 coupled with 695  $\text{cm}^{-1}$  is

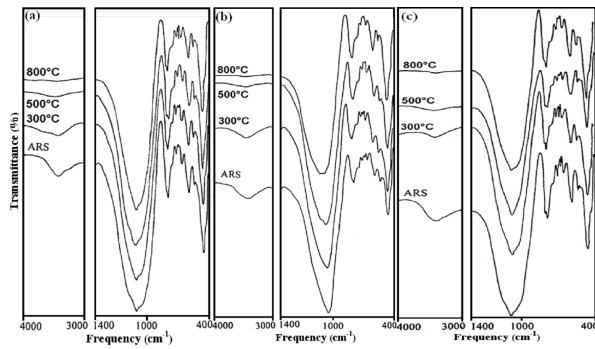


Fig. 2. Room temperature FTIR absorption spectra of pottery sherds in the as received state (ARS) and at different refring temperatures of Perumalpattu (a) PMU-1, (b) PMU-3, (c) PMU-4.

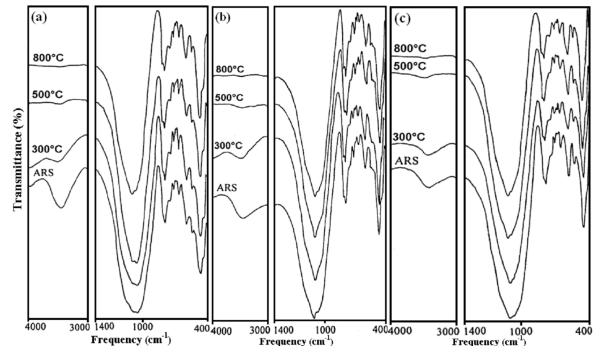


Fig. 3. Room temperature FTIR absorption spectra of pottery sherds in the as received state (ARS) and at different refring temperatures of Theriruvveli (a) TRI-1, (b) TRI-3, (c) TRI-4.

an indication of presence of quartz. Pottery sherds collected from Perumalpattu and Theriruvveli contain quartz as predominant and make the clay self-tempered.

In order to estimate the firing temperature of any clay-based materials above 600 °C, the presence or absence of certain bands can serve as thermometer especially the absorption bands at 580 and 540  $\text{cm}^{-1}$ , which are attributed to iron oxides [15]. The amounts of iron oxides decide about the reducing or oxidizing or changing atmosphere used for firing the artifacts [16–18]. The method of firing is very important 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]. The FTIR spectra of PMU-1, PMU-2, PMU-4, PMU-5, PMU-7, TRI-2, TRI-3, TRI-4, TRI-5, TRI-6, TRI-7, show absorption due to hematite (580  $\text{cm}^{-1}$ ) indicating that these samples have been fired in open air or perfectly oxidising atmosphere at the time of manufacture. Also, the FTIR absorption spectra of the above potteries obtained as received state are similar as the spectra of the same sherds refired in the laboratory at 300, 500, and 800 °C. This indicates that the laboratory refring temperature does not exceed the original firing temperatures of the sherds, whereas in the case of pot-

tery sherds PMU-3, PMU-6, PMU-8, TRI-1 and TRI-8 the FTIR absorption spectra obtained in the as received state are similar as one obtained at 300 °C and 500 °C (see the peak position and intensity of the bands at 540 and 580  $\text{cm}^{-1}$ ). At 800 °C, a change is observed i.e., the intensity of the band 580  $\text{cm}^{-1}$  has increased. This indicates that the above sherds while manufacturing, have been fired under strongly reducing atmosphere with charcoal and wood but reoxidation takes place while fired in the laboratory in air. Wagner et al. [21] have reported that when previously reduced material is heated in air, reoxidation process will take place in between about 450 and 600 °C, resulting an increase or decrease in the intensity of iron oxides.

Iron, generally present in unpurified clay materials in concentrations of several percent in the form of oxides, is the key factor to understand the colour of the potteries. The colour of the pottery is due to the content of iron oxides which act as the colouring agent. Velraj et al. [5] have reported that the colour of the potteries is due to hematite which is a red brown solid and it decides the atmospheric conditions (oxidizing/reducing) where the artifacts are fired. The potteries collected from Perumalpattu, namely, PMU-1, PMU-2, PMU-4, PMU-5, PMU-7 and Theriruvveli, TRI-2, TRI-3, TRI-4, TRI-5, TRI-6 and TRI-7 are red and reddish brown in colour and show the presence of hematite fired in the oxidizing atmosphere. The black coloured potteries of PMU-8 and TRI-8 have been probably fired in the reducing atmosphere. Red colour surface and black colour core of pottery sherds PMU-6 and TRI-5 may be due to the adoption of changing atmosphere during heating and cooling the potteries in the kiln at the time of manufacture. According to Wagner et al. [22], the estimation of firing temperature of black and multicoloured sherds are very critical because when refring the sherds in the laboratory, reoxidation takes place above 450 °C. Estimated firing temperature and firing atmosphere through FTIR technique are summarized in Table I.

Further, it is important to note that the FTIR absorption spectra of local clay materials of Perumalpattu and Theriruvveli studied at different temperatures in the laboratory are entirely different at higher temperatures (see the peak position and intensities of the band 580 and 540  $\text{cm}^{-1}$ ). It is found that the presence of iron compounds in Theriruvveli clay materials is very low, whereas in Perumalpattu clay material it is sufficient. The FTIR spectra of few pottery sherds (PMU-1, PMU-3, PMU-4, TRI-1, TRI-3, TRI-4) collected from Perumalpattu and Theriruvveli are almost identical to that of the Perumalpattu clay material studied at different temperature in the laboratory. This indicates the translocation of Perumalpattu pottery artifacts to Theriruvveli during the archaeological period. So, one can understand that North and South regions of Tamilnadu State have had the trade link in the archaeological past and hence the archaeologists' views of Government of Tamilnadu State are confirmed.

#### 4.2. Mössbauer measurements of archaeological pottery sherds

The wide applicability of <sup>57</sup>Fe Mössbauer spectroscopy for investigations of clay-based products arises from the fact that practically all clays contain iron, usually in concentrations between 1 and 10 weight percent. Natural iron contains about 2% of the <sup>57</sup>Fe isotope used in Mössbauer spectroscopy and this is sufficient for measuring good Mössbauer spectra of most clay-based products [21]. During firing of clay products, iron undergoes characteristic changes of chemical and physical state, depending on the kiln atmosphere, and on the maximum firing temperature is reached. These changes can be followed by the Mössbauer spectroscopy [2].

The Mössbauer spectra of ancient pottery have been first reported by Cousins and Dharmawardena [23]. Work

up has been reviewed by Kostikas et al. [24] and then by Venkatachalapathy et al. [25]. The physical and chemical state of iron oxide phases and their interactions with the other constituents of clay correlate with colour and texture of the pottery [26, 27] and can be associated with major parameters of the manufacturing procedure as, e.g., firing temperature and atmosphere.

Iron in clay appears (i) in the form of paramagnetic ions (ferric Fe<sup>3+</sup> or ferrous Fe<sup>2+</sup>) substituting Al or (less frequently) Si sites in the clay minerals, and (ii) in the form of magnetic iron oxides or hydroxides usually dispersed as small particles with sizes of the order of 100 Å [28]. Figures 4 and 5 display a typical room temperature Mössbauer spectrum of different coloured pottery sherds of Perumalpattu and Theriruvveli with spectral features corresponding to the iron phases mentioned above.

TABLE I

Estimated firing temperature and firing atmosphere of the pottery sherds excavated at Perumalpattu (PMU) and Theriruvveli (TRI).

Sample No.	Colour	Presence of iron component	Estimated firing temperature	Estimated firing atmosphere
PMU-1	red	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
PMU-2	red	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
PMU-3	black	–	–	reducing
PMU-4	red	Fe <sub>2</sub> O <sub>3</sub>	750 ± 50 °C	oxidizing
PMU-5	reddish brown	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
PMU-6	red and black	–	–	changing
PMU-7	red	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
PMU-8	black	–	–	reducing
TRI-1	black	–	–	reducing
TRI-2	red	Fe <sub>2</sub> O <sub>3</sub>	750 ± 50 °C	oxidizing
TRI-3	red	Fe <sub>2</sub> O <sub>3</sub>	750 ± 50 °C	oxidizing
TRI-4	red	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
TRI-5	red	Fe <sub>2</sub> O <sub>3</sub>	750 ± 50 °C	changing
TRI-6	reddish brown	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
TRI-7	reddish brown	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	> 850 ± 50 °C	oxidizing
TRI-8	black	–	–	reducing

From Table II it is observed that the common component in the room temperature Mössbauer spectra of all the pottery sherds is the doublet (*A*) which has  $\Delta = 0.86$ – $1.21$  mm/s and  $\delta = 0.38$ – $0.45$  mm/s. These values are characteristic of ferric irons (Fe<sup>3+</sup> species) in octahedral sites in silicates. It can be due to the presence of kaolinite. FTIR studies confirm the presence of kaolinite mineral in the clay materials of Perumalpattu and Theriruvveli. The value of magnetic hyperfine field and the quadrupole splitting of magnetic pattern appearing in the Mössbauer spectra of pottery sherds PMU-1, PMU-2, PMU-4, PMU-5, PMU-7 and TRI-2,

TRI-3, TRI-4, TRI-5, TRI-6 and TRI-7 indicate that this component is due to Fe<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> mixed with the clay or adhering to its surface. These results are confirmed by FTIR studies, which show the presence of Fe<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the above sherds and the presence of Si–O groups in all sherds.

The relative spectral area of the component due to Fe<sub>2</sub>O<sub>3</sub> constitutes 45 to 75% of the total iron present in sherds PMU-1, PMU-2, PMU-5, PMU-7, TRI-4, TRI-6 and TRI-7. This result is in agreement with the reddish colour of these sherds which is found to be mainly due to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. According to Wagner et al. [9, 22],

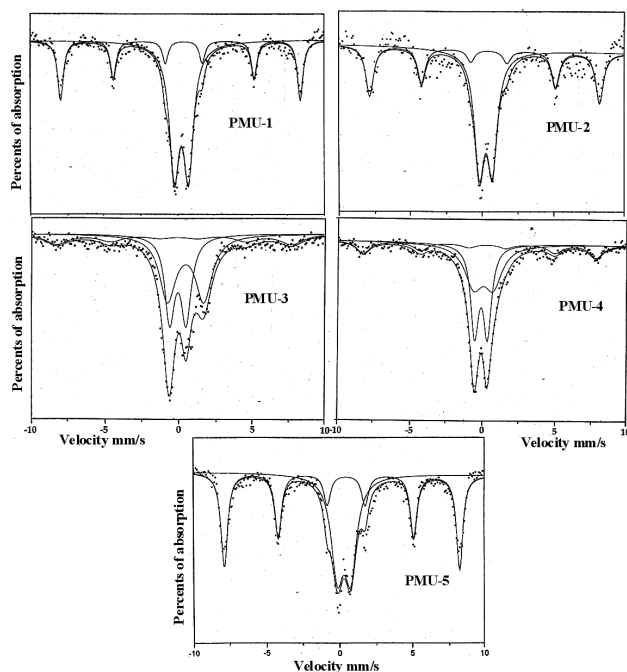


Fig. 4. Room temperature Mössbauer spectra of the pottery sherds of Perumalpattu.

the quadrupole splitting exhibits a substantial increase on firing between 350 and 500 °C due to the distortion of the octahedral symmetry of the iron sites during the dehydroxylation process in the clay minerals. Following the dehydroxylation of clay minerals, the quadrupole splitting of octahedrally coordinated  $\text{Fe}^{3+}$  ions increases abruptly from 0.66 mm/s in fresh clay to 1.05 mm/s on firing at 400 °C. The splitting may reach up to 1.35 mm/s on firing at around 750 °C. The quadrupole splitting values revert to lower values upon the formation of new, better ordered phases at higher temperatures (possibly above 750 °C). The authors have also reported that hematite formation is possible above 750 °C.

From these information, in the present study, the obtained quadrupole splitting values of the doublet correspond to  $\text{Fe}^{3+}$  ions allowing us to infer a rough estimation of the firing temperature as above 800 °C for the sherds PMU-1, PMU-2, PMU-5, PMU-7, TRI-2, TRI-4, TRI-6 and TRI-7. The pottery sherds PMU-4, TRI-2, TRI-3 and TRI-5 might be fired in between 700 °C and 800 °C. The presence of a higher amount of  $\text{Fe}^{2+}$  ions in the pottery sherds PMU-3, PMU-6, PMU-8, TRI-1 and TRI-8 indicates that they have been subjected to a strong reducing atmospheric firing during manufacturing in the archaeological past.

According to Ramaswamy et al. [29] and Venkatachalapathy et al. [30], the presence of higher percentage of  $\text{Fe}^{2+}$  reveals the reduced atmosphere and is the reason for black colour of the pottery, whereas higher percentage of  $\text{Fe}^{3+}$  is due to the strong oxidizing atmosphere which reflects reddish colour of the pottery. The authors have also reported that the magnetic hyperfine field value of

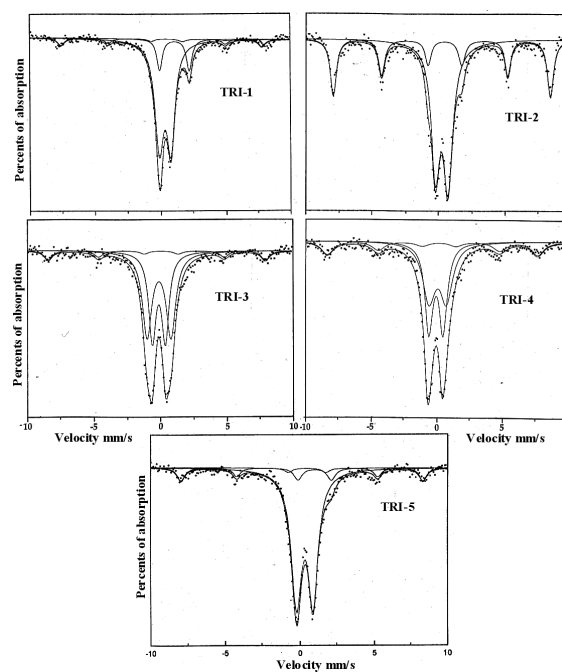


Fig. 5. Room temperature Mössbauer spectra of the pottery sherd of Theriruvveli.

508–510 kOe is attributed to the presence of hematite. In the present work, it is observed that black colour sherds PMU-3, 6, and 8, TRI-1 and TRI-8 contain around 60% of  $\text{Fe}^{2+}$  species and no  $\text{Fe}_2\text{O}_3$ , while red colour sherds contain higher percentage of  $\text{Fe}_2\text{O}_3$  and sufficient amount of  $\text{Fe}^{3+}$  species. Based on these observations, it is established that the presence of  $\text{Fe}_2\text{O}_3$  and the adoption of oxidizing atmospheric firing are the reasons for the reddish colour of the pottery sherds collected from Perumalpattu and Theriruvveli, whereas black colour corresponds to reduce atmospheric firing using charcoal and wood. The presence of black and red colours on the pottery sherds studied may be attributed to the blow of air in the closed kiln during the process of firing at reduced atmosphere.

The black colour pottery sherds and TRI-1 and TRI-8 have shown the presence of higher amount of ferrous compounds attributed to the reducing conditions in the kiln during firing. These ferrous compounds together with carbon from dense smoke are the causes for the black colour. Coey et al. [31] have proved that control of firing atmosphere could produce a black colour and attributed it to the non-magnetic ferrous oxide FeO. So, the absence of  $\text{Fe}_2\text{O}_3$  in the spectra of the pottery sherds (PMU-3, PMU-6, PMU-8 and TRI-1 and TRI-8) may be due to the reduction of the ratio of the ferric to the ferrous oxides.

Further, the Mössbauer spectra of pottery sherds collected from Perumalpattu, namely PMU-1, PMU-2, PMU-4 and from Theriruvveli TRI-2 and TRI-4 are almost identical and may have the same origin and confirm the archaeologists views about these potteries in the Tamilnadu State, India. The results obtained for pottery sherds through Mossbauer Spectroscopy are summarized in Table III.

TABLE II

Room temperature Mössbauer parameters of investigated sherds.

Sample No.	Components	Colour	Trench No.	Fe <sup>2+</sup>		Fe <sup>3+</sup>		Fe <sub>2</sub> O <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>		H [kOe]	I <sub>rel</sub> [%]		
				δ [mm/s]	Δ [mm/s]	δ [mm/s]	Δ [mm/s]	δ [mm/s]	Δ [mm/s]		Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sub>2</sub> O <sub>3</sub>
PMU-1	bulk	red	02	–	–	0.38±0.03	0.99±0.01	0.44±0.03	–0.21±0.02	507±2	–	45±1	55±2
PMU-2	bulk	red	02	–	–	0.38±0.03	0.98±0.01	0.45±0.03	–0.23±0.02	507±2	–	47±1	53±2
PMU-3	bulk	black	02	1.15±0.04	2.39±0.03	0.41±0.03	1.21±0.01	–	–	–	62±1	38±1	–
PMU-4	bulk	red	02	–	–	0.44±0.03	1.10±0.01	0.61±0.04	–0.49±0.02	496±2	–	88±3	12±1
PMU-5	bulk	reddish brown	04	–	–	0.42±0.03	0.87±0.01	0.42±0.03	–0.20±0.03	512±5	–	28±1	72±2
PMU-6	surface core bulk	red black black	04	1.07±0.03	2.27±0.03	0.47±0.03	0.91±0.01	–	–	–	60±1	40±1	–
PMU-7	bulk	red	04	–	–	0.39±0.03	0.97±0.01	0.38±0.03	–0.21±0.02	509±3	–	43±1	57±2
PMU-8	bulk	black	04	1.09±0.03	2.34±0.03	0.40±0.03	0.86±0.01	–	–	–	65±1	35±1	–
TRI-1	bulk	black	01	1.18±0.04	2.30±0.03	0.44±0.03	0.90±0.01	–	–	–	56±1	42±1	–
TRI-2	bulk	red	01	–	–	0.43±0.03	1.15±0.01	0.46±0.03	–0.31±0.02	492±2	–	91±3	09±1
TRI-3	bulk	red	03	–	–	0.43±0.03	1.18±0.01	0.40±0.03	–0.45±0.03	495±2	–	86±3	14±2
TRI-4	bulk	red	03	–	–	0.39±0.03	0.91±0.01	0.44±0.03	–0.28±0.02	505±3	–	43±1	57±2
TRI-5	surface core bulk	red black red	03	1.11±0.04	2.30±0.03	0.44±0.03	1.15±0.01	0.46±0.03	–0.30±0.03	494±2	–	87±3	8±1
TRI-6	bulk	reddish brown	04	–	–	0.38±0.03	0.86±0.01	0.43±0.03	–0.21±0.02	511±5	–	25±1	75±2
TRI-7	bulk	reddish brown	04	–	–	0.39±0.03	0.86±0.01	0.41±0.03	–0.24±0.03	514±5	–	29±1	71±2
TRI-8	bulk	black	04	1.10±0.04	2.33±0.03	0.45±0.03	0.93±0.01	–	–	–	70±1	30±1	–

δ — isomer shift, Δ — electric quadrupole splitting, H — magnetic hyperfine field in kOe, I<sub>rel</sub> — relative spectral area.

TABLE III

The correlation of % content of Fe<sup>2+</sup>/Fe<sup>3+</sup>/Fe<sub>2</sub>O<sub>3</sub> with the colour and estimated firing temperature and nature of firing of the pottery sherds obtained from Perumalpattu and Theriruvveli.

Sample No.	Colour	Constituent [%]			Estimated firing temperature in °C	Estimated firing atmosphere
		Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sub>2</sub> O <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>		
PMU-1	red	–	45	55	> 850 ± 50 °C	oxidizing
PMU-2	red	–	47	53	> 850 ± 50 °C	oxidizing
PMU-3	black	62	38	–	–	changing
PMU-4	red	–	88	12	750 ± 50 °C	oxidizing
PMU-5	reddish brown	–	28	72	> 850 ± 50 °C	oxidizing
PMU-6	red and black	60	40	–	–	changing
PMU-7	red	–	43	57	> 850 ± 50 °C	oxidizing
PMU-8	black	75	25	–	–	reducing
TRI-1	black	56	44	–	–	changing
TRI-2	red	–	91	09	750 ± 50 °C	oxidizing
TRI-3	red	–	86	14	750 ± 50 °C	oxidizing
TRI-4	red	–	43	57	> 850 ± 50 °C	oxidizing
TRI-5	red	–	87	08	750 ± 50 °C	oxidizing
TRI-6	reddish brown	–	25	75	> 850 ± 50 °C	oxidizing
TRI-7	reddish brown	–	29	71	> 850 ± 50 °C	oxidizing
TRI-8	black	70	30	–	–	reducing

## 5. Conclusion

The main subject of this investigation is to find the translocation of the pottery from Perumalpattu to Theriruvveli with the determination of firing temperature and firing atmosphere. Pottery sherds excavated from Perumalpattu and Theriruvveli have been made up of red

clay material. It is estimated that pottery sherds PMU-1, PMU-2, PMU-5, PMU-7, TRI-4, TRI-6 and TRI-7 were fired above 800 °C and PMU-4, TRI-2, TRI-3 and TRI-5 in the range of 700–800 °C. The estimation of firing temperature of black and multicoloured pottery sherds are very difficult because during refiring the sherds in the laboratory, re-oxidation takes place in between 450

and 600°C. The identical FTIR and Mössbauer spectra of few pottery sherds of Perumalpattu and Theriruvelli indicate that there have been trading links between North and South regions of Tamilnadu State in the ancient past. Also, the artisans living at that time were well aware of using the technology of firing (oxidising, reducing and changing atmosphere of the kiln) for producing good quality (by firing in between 700–800 and above 800°C) and different coloured potteries for different domestic purposes like storing water, food grains and cooking.

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