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Estimation of firing temperature and ancient geomagnetic field intensity of archaeological potteries recently excavated from Tamilnadu, India

G. Velraj [a,*], A. Mohamed Musthafa [a], K. Janaki [a], K. Deenadayalan [b], N. Basavaiah [b]

[a] Department of Physics, Periyar University, Salem 636011, India
[b] Environmental Magnetism Laboratory, Indian Institute of Geomagnetism, Navi Mumbai 410218, India

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ABSTRACT

In the present study, fragmented pottery samples were collected from the recently excavated archaeological site named Salamankuppam near the famous Mahabalipuram in Chennai, Tamilnadu, India. An attempt was made to subject the samples to scanning electron microscope with energy dispersive spectrometer (SEM/EDS) and chemical analysis. Also porosimetry study was done. The result from the analysis provided the chemical composition of the potteries, the firing atmosphere and firing temperature achieved by the artisans at the time of manufacture. The results obtained from different analytical techniques provided information of the firing temperature of the pottery which lies in the range of 800 °C–950 °C in the oxidizing and reducing atmosphere. Mineral magnetic studies also were performed and proved that all samples were highly magnetically enhanced materials and paleointensity measurements by Thellier method yielded the field intensity value of 42.15 ± 2.0 μT. The age of the sample was around 150 BC.

1. Introduction

Pottery is one of the most enduring materials known to mankind. In most places, it is the oldest and the most widespread art because pottery is a durable artifact that was utilized by various cultures around the world. The study of pottery helps to identify the different cultural groups and their influence on one another (Manoharan et al., 2008). Pottery is very helpful for identification of a civilization and it throws light on ancient people's life. The clays usually carry stable remanent magnetization materials such as iron oxides, which has fossilized in the direction and intensity of the geomagnetic field at the time and in the place when the material was last fired (Kovacheva et al., 1998; Manoharan et al., 2008). In the present study, the samples were collected at Salamankuppam, Tamilnadu, India. Various techniques such as FT-IR, chemical analysis, SEM-EDS and porosimetry studies were employed to estimate the firing temperature and production technology. Mineral magnetic parameters such as susceptibility, Q-ratio and S-ratio indicated the presence of highly enhanced magnetic material present in the sample and helps to estimate the ancient geomagnetic field intensity.

2. Site details

The site Salamankuppam (12° 36′ N 80° 11′ E) is about 1.5 km north of the famous shore temple Mahabalipuram and 150 m from the sea. The site was excavated by the Archaeological Survey of India (ASI). Mahabalipuram is a wonder showpiece of marvel of Pallava art and architecture. It was once a flourishing seaport by maintaining brisk trade with countries in south-east Asia and the Mediterranean in the Pallava dynasty. Mahabalipuram with its natural heritage is a fine seacoast together with abundant man-made historical and architectural monuments. The geological map of the excavated archaeological site is shown in Fig. 1.

3. Experimental details

Fragmented pottery pieces were collected at the archaeological site Salamankuppam in the state of Tamil Nadu, India. Water absorption (Palanivel and Velraj 2003; Velraj et al. 2009a,b) was adopted to measure the porosity values of the pottery samples. The microphotographs of the samples were recorded using SEM JSM 561OLV JEOL. The maximum magnification possible in the equipment was 300,000 times with the resolution of 3 nm. The elemental analysis was done using the OXFORD INCA Energy Dispersive X-ray spectrometer (EDS). The fresh fracture surfaces of the potteries in the received state (ARS) coated with a thin layer of gold were examined by SEM, typically setting at a magnification of ×2000 for all the samples. The microphotographs were recorded with the attached accessories of high-resolution cathode ray tube and a role film camera (Mirti et al., 2006). Titration was adopted to find the chemical composition of potteries (Table 1) for chemical analysis (John Maxwell, 1968).

* Corresponding author. Tel.: +91 427 2345766x247; fax: +91 427 2345565.
E-mail address: gvelraj@yahoo.co.uk (G. Velraj).

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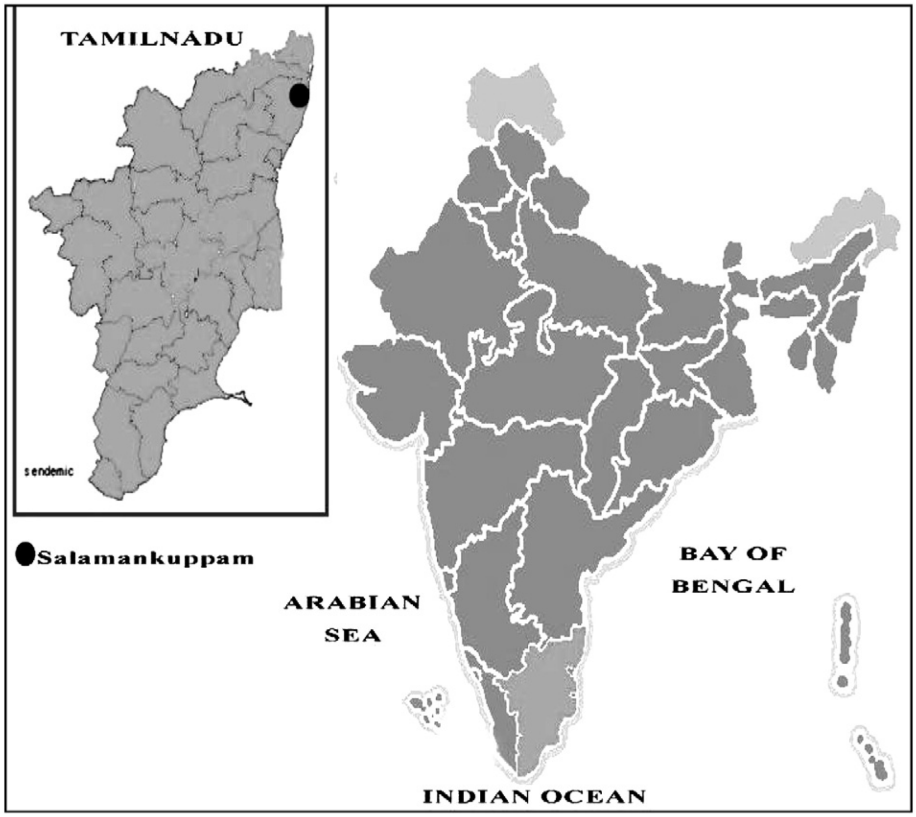

Fig. 1. Archaeological site of recent excavation (•) in Tamilnadu, South India.

3.1. Mineral magnetic studies

The mass-specific magnetic susceptibility was measured at $\chi_{LF}=$ 0.47 kHz and $\chi_{HF}=4.7$ kHz with a Bartington MS2B dual-frequency susceptibility meter with an accuracy of 1×10^{-5} SI unit by applying the field strength of 80 A/m. The frequency-dependent magnetic susceptibility $\chi_{FD}=((\chi_{Lf}-\chi_{HF})/\chi_{LF})\times100$ in % was calculated. Isothermal remanence was induced using MOLSPIN pulse magnetizer, UK. Magnetizations were measured with MINISPIN spinner magnetometer (MOLSPIN Ltd., UK) with an accuracy of 2.4×10^{-6} A/m. The modified Thellier and Thellier method was used to obtain the paleointensity values. Thermal demagnetization was carried out using magnetic measurement thermal demagnetizer (MMTD, UK).

4. Results and discussion

4.1. Firing temperature estimation by chemical analysis

The chemical composition can be used to define the pottery of a particular area and people by determining the raw materials used. Chemical analysis was performed to know the type of clay minerals (calcareous/non-calcareous and either low or high refractory) and to determine the firing atmosphere adopted by the artisans at the time of manufacture. Calcareous or non-calcareous were identified by the content of calcium oxide (CaO). According to Maniatis and Tite (1981) the clays containing >6% CaO, are known as calcareous clays and with <6% as non-calcareous clays. If the content of fluxes (K_2O, Fe_2O_3, CaO, MgO and TiO_2) are >9%, the clays are classified as low refractory clays From the ratio of iron oxides (magnetite and hematite) in the sample the atmospheric condition during firing can also be identified. If the amount of magnetite in the sample is large, it may have been fired at reducing atmosphere (De Benedetto et al., 2002). If the amount of hematite is high, the atmosphere was oxidizing (Maniatis and Tite, 1981).

The high silica content is caused by the presence of quartz. Next to silica, the most abundant important elements are Al, Ti, K, Mg, Fe and

Table 1
Chemical composition of archaeological pottery shreds of the Salamankuppam site by chemical analysis.

Chemical composition (mass%)	SSM1	SSM2	SSM3	SSM4	SSM5
SiO_2	55.42	57.43	63.86	63.38	58.68
Al_2O_3	14.94	19.06	18.49	15.52	16.92
K_2O	2.34	4.68	3.63	2.01	3.34
Fe_2O_3	6.77	9.19	5.18	7.15	6.23
CaO	3.38	1.40	2.26	3.26	1.44
MgO	1.34	0.97	0.63	0.39	0.60
TiO_2	1.25	1.45	BDL	1.06	1.32
Fe_3O_4	6.37	6.34	7.51	4.93	9.02

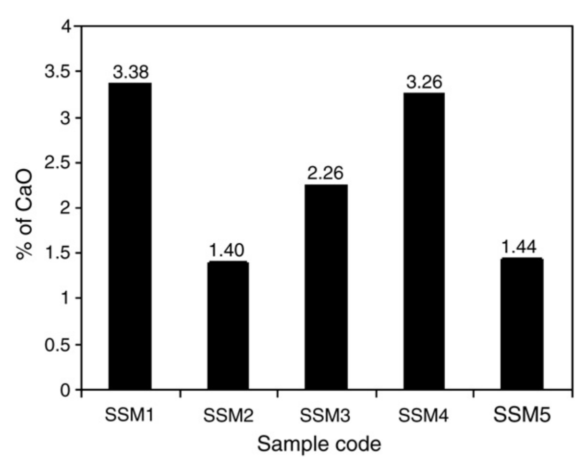

Fig. 2. Variation of CaO in the pottery samples.

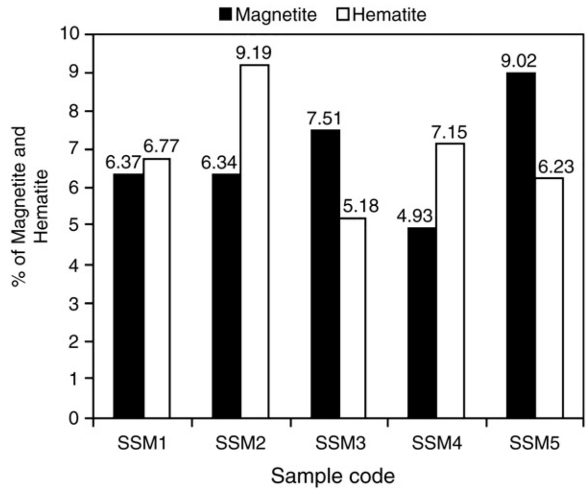

Fig. 3. Variation of hematite and magnetite in the pottery samples.

Ca. The content of CaO ranges from 1.40 to 3.38% indicating non-calcareous type (Fig. 2). The content and distribution of the iron oxides are the principal causes for color of the potteries. The red color of the pottery is due to the presence of hematite and the black color is due to higher amounts of magnetite (Mirti et al., 2006; Mirti and Davit, 2004; Yariv and Mendelovici, 1979). Here an attempt was made to correlate the color of the potteries with the state of iron. The ratio of magnetite to hematite was observed to be very low in SSM1, SSM2 and SSM4. As the samples SSM3 and SSM5 had low hematite contents and were black, they were fired in reducing atmosphere (Fig. 3).

The samples collected were low refractory clays. Only the people belonging to Salamankuppam site knew the art of firing in closed kiln. Hence the performed chemical analysis provided useful information about the analytical composition of the specimen. This first fundamental step in the knowledge of the artifacts leads to considerations about the manufacture technique.

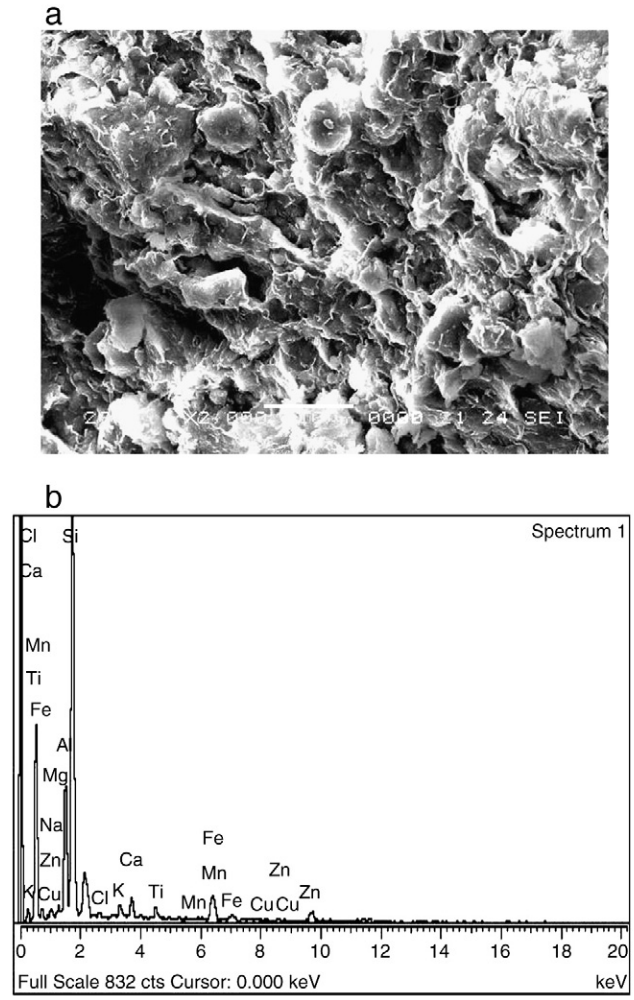

Fig. 4. a. Microphotograph of SSM1. b. EDS spectrum of SSM1.

4.2. Firing temperature estimation by SEM-EDS

The elemental concentrations of the potteries examined under SEM, along with EDS, are given in Table 2. The EDS clearly indicated low refractory clays (Maniatis and Tite, 1981) and all the samples had high iron contents in agreement with the chemical analysis and mineral magnetic parameters.

The sample SSM1 did not show vitrification (Fig. 4a), from the elemental analysis (Fig. 4b) shows, it is of the non-calcareous type. According to Maniatis and Tite (1975), low refractory non-calcareous clays produced in oxidizing condition with no vitrification stage were fired <800 °C. The samples SSM2 and SSM4 showed extensive vitrification (EV). The elemental analysis showed that these samples are of non-calcareous type. Whether calcareous or non-calcareous low refractory clays fired in oxidizing condition with EV were fired at 850–950 °C (Maniatis and Tite, 1975). Accordingly all samples were fired at 850–950 °C. However, the sample SSM5 showed extensive vitrification and is a low refractory, non-calcareous clay but fired in reducing atmosphere, and hence it might had been fired at 800–900 °C. SSM3 was in a continuous vitrification stage and is a low refractory non-calcareous clay fired in reducing atmosphere, and hence it may have been fired at 850–950 °C. The estimated firing temperature by SEM analysis is shown in Table 3.

Table 2
Chemical composition of archaeological pottery shreds of the Salamankuppam site by EDS analysis.

Chemical compositions (mass %)	SSM1	SSM2	SSM3	SSM4	SSM5
MgO	0.91	0.46	0.83	0.94	0.76
Al_2O_3	14.53	20.73	19.27	14.77	16.46
SiO_2	56.40	57.03	60.40	64.02	55.49
K_2O	2.25	4.93	3.46	2.04	3.68
CaO	4.23	1.04	2.09	3.11	2.06
TiO_2	2.76	1.78	–	1.31	1.21
FeO	14.59	13.34	11.77	11.80	16.65

4.3. Porosity measurements

The physical appearance such as color, nature of particle and porosity values and the estimated firing temperature of the archaeological pottery shreds is shown in Table 3.

The porosity values varied from 22 to 46%. The samples SSM1 and SSM5 had low porosity (27 and 25%) compared to SSM2–SSM4 (44, 46, and 38%). According to Palanivel and Velraj (2003) and Velraj et al. (2009a,b), the samples SSM1 and SSM5 contain fine particles and were fired <900 °C and the remaining samples contained coarse particles and hence were fired <1000 °C. The estimated firing temperature coincides with that of SEM analysis.

4.4. Magnetic studies

4.4.1. Magnetic susceptibility

Magnetic susceptibility describes the magnetic property of the sample when exposed to weak magnetic field. Magnetic susceptibility

Table 3
Determination of firing temperature derived from SEM with EDS and porosity measurements.

Sample code	Color	C/NC	Particle nature	Porosity (%)	Estimated temperature by porosity measurement	Vitrification	Atmosphere prevailed	Estimated temperature by SEM analysis
SSM1	Red ware	NC	Fine	27	<900 °C	NV	Oxidizing	<800 °C
SSM2	Red slipped ware	NC	Coarse	44	<1000 °C	EV	Oxidizing	850–950 °C
SSM3	Black ware	NC	Coarse	46	<1000 °C	CV	Reducing	850–950 °C
SSM4	Red ware	NC	Coarse	38	<1000 °C	EV	Oxidizing	850–950 °C
SSM5	Red and black ware	NC	Fine	25	<900 °C	EV	Reducing	800–900 °C

NC—non-calcareous; C—calcareous; NV—no vitrification; EV—extensive vitrification; CV—continuous vitrification.

is a function of concentration as well as the mineralogy of the ferromagnetic minerals like magnetite, maghemite etc (Mooney et al., 2002). In the present study, the magnetic susceptibility χ of pottery samples spread over a wide interval $6–40\times10^{-7}$ m^3/kg (Fig. 5) indicating a large magnetic enhancement. Basically, archaeological samples show very high magnetic susceptibility because of high temperature at the time of manufacture. Dunlop and Ozdemir (1997) and Thompson and Oldfield (1986) reported that the magnetic susceptibility mainly depends on the content of ferrimagnetic minerals. Values of χ_{FD} indicate the presence of very fine metastable magnetic grains spanning the super paramagnetic (SP), single domain (SD) boundary (Worm, 1998). All the samples except SSM1 showed χ_{FD} between 5 and 10%, indicating the presence of SP grains.

4.4.2. Koenigsberger ratio (Q-ratio)

Koenigsberger ratio is a magnetic parameter related to the two most important parameters NRM and χ. From these two parameters, Q-ratio is calculated by dividing the natural remanent magnetization (NRM) by the induced magnetization. The magnetization value is 0.5 Oe, which corresponds to a magnetizing force of 39.79 A/m (McElhinny and Senanayake, 1982).

The Q-ratio of the pottery samples provides the information about the type of minerals and their domain state that produce induced remanent magnetization. High Q-ratio values are the characteristics of stable natural remanent magnetization The remanence is dominant for $Q>1$ (Alva-Valdivia et al., 2003). Variation of NRM and susceptibility mainly depends on the volume content of magnetite. $Q>1$ indicates the presence of single domain/pseudo-single-domain magnetic grains in the samples. All pottery samples showed $Q>1$ except SSM1 (Fig. 6).

4.4.3. Soft and hard isothermal remanent magnetization (IRM)

Soft and hard isothermal remanent magnetization (IRM) also indicate the type of magnetic minerals. High values of soft IRM show the presence of higher amount of ferrimagnetic grains than of anti-ferromagnetic grains (Basavaiah and Khadkikar, 2004). SSM2–SSM5 showed high values of soft IRM whereas SSM1 contained equal proportion of ferrimagnetic and anti-ferromagnetic minerals.

Thus, all the samples except SSM1 showed good stable remanent magnetization (Fig. 7) and were more suitable for estimating the paleointensity field value.

4.4.4. Paleointensity measurements

Most paleointensity determination using archaeological artifacts like pottery, bricks and tiles and lava flow is mainly based on the classical Thellier and Thellier method (Thellier and Thellier, 1959) or its modification (Coe 1976; Kono and Ueno 1977). The paleointensity fossilized in the baked materials can be retrieved through archaeomagnetic investigation (Manoharan et al., 2008). The modified Thellier and Thellier method involves heating the sample at zero field increasing temperature (75 °C to 600 °C in steps of 25 °C) and measuring the NRM intensity. After removing the total magnetization, the heating process is

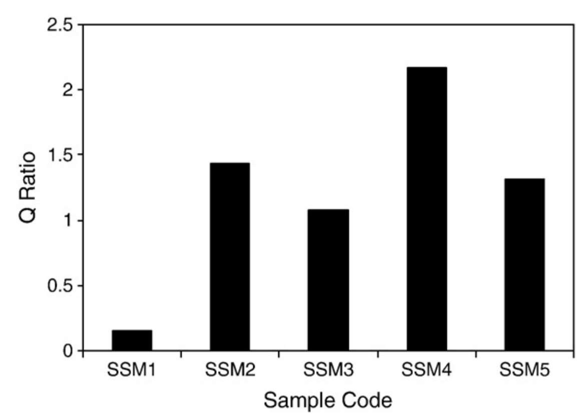

Fig. 6. Q-ratio vs archaeological artifacts.

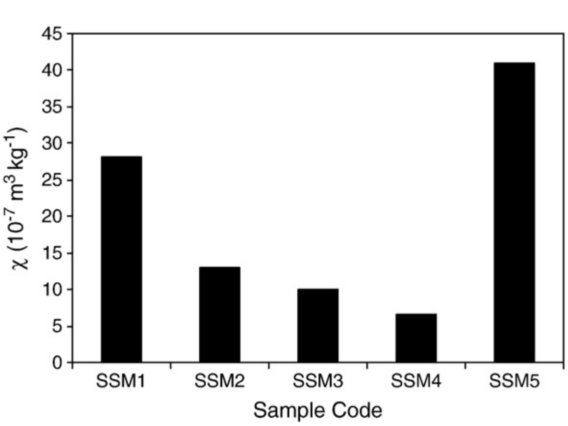

Fig. 5. Susceptibility vs archaeological artifacts.

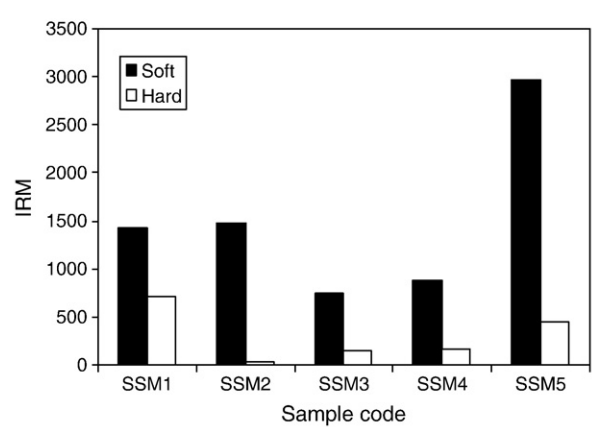

Fig. 7. IRM vs archaeological artifacts.

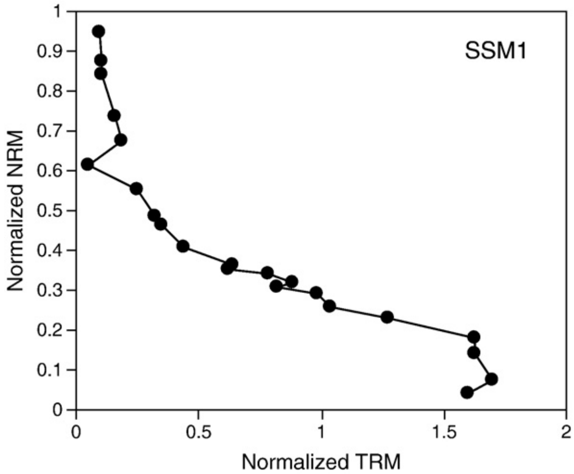

Fig. 8. Arai plot of SSM1.

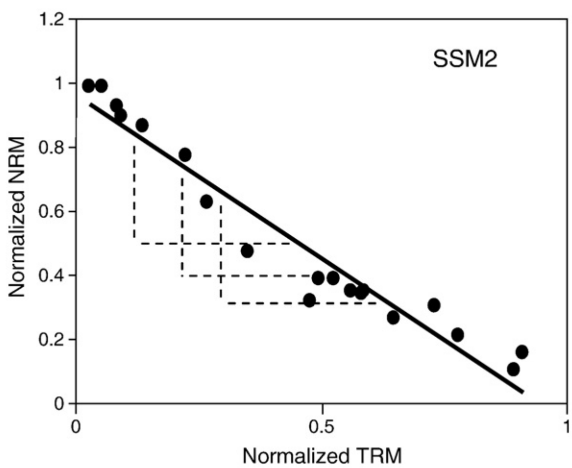

Fig. 9. Arai plot of SSM2.

repeated at the same temperatures but the sample is exposed to the known reference field and its thermo remanent magnetization (TRM) is measured. The Arai plots of the rejected sample (SSM1) and good sample (SSM2) are shown in Figs. 8 and Fig. 9. The slope of the best fitting line to the linear part of the Arai diagram multiplied by the laboratory field value gives the intensity of ancient geomagnetic field,

$$B_{anc} = (NRM \,/\, TRM) \times B_{lab}\ (\mu\mathrm{T}).$$

The paleointensity of all the samples was 42.15 ± 2.0 μT. B_{anc} was determined from the pre-drawn secular variation curve (Ramaswamy and Duraiswamy, 1990), the age of the sample was 150 BC, and coincided with the date predicted by the archaeologist. Fig. 10 represents the secular variation of South India, and the age of the Salamankuppam site is marked in the curve.

5. Conclusions

The quantitative analysis confirmed that the samples were rich in fluxes, and more significantly, the amounts of hematite and magnetite indicated the firing atmosphere at the time of manufacture. These findings were supported by the EDS analysis. The artisans of this site knew the art of firing in oxidizing and reducing atmosphere and used both fine and coarse particles for potteries. The firing temperature estimated by porosity measurements also coincided with that of the SEM analysis. The magnetic study of all the pottery samples except SSM1 reflected the magnetic structure, grain size and concentration. The specific susceptibility indicated a high magnetic enhancement in the samples. The frequency-dependent magnetic susceptibility χ_{FD} indicated the presence of significant amounts of super paramagnetic domains. Q-ratio values reflected the presence of pseudo-single domains. The soft and hard isothermal remanent magnetization indicate the presence of high concentration of ferromagnetic minerals. Thus, all the pottery samples showed stable remanence except SSM1, the ancient geomagnetic field intensity was 42.15 ± 2.0 μT. The age predicted from this study was in good agreement with the archaeological reference data.

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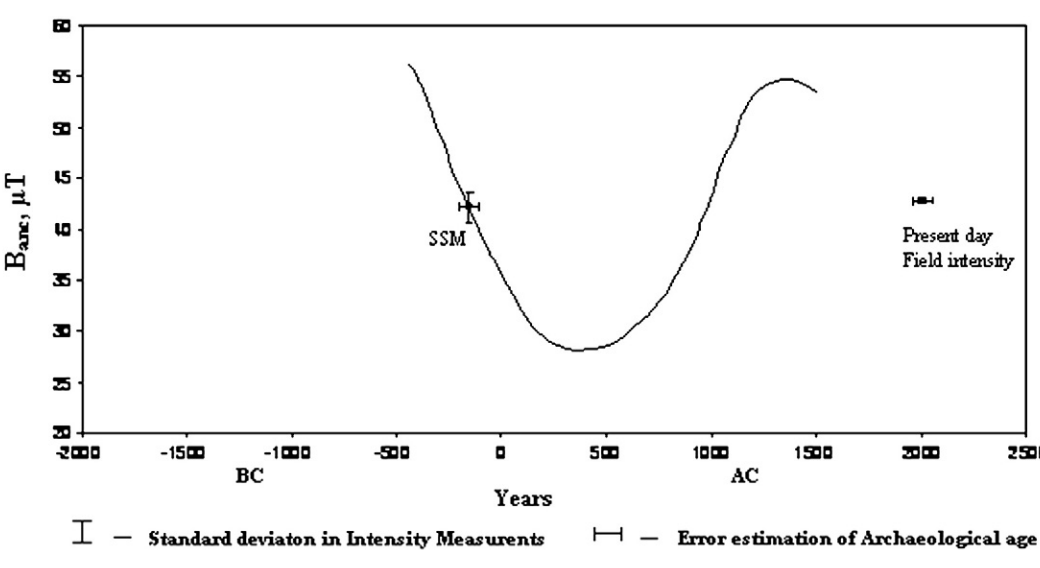

Fig. 10. Secular variation curve of South India indicating the age of the samples.

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