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Investigations on Ancient Pottery Samples by Proton Induced X-Ray Emission Using Protons of Energy 2.5 MeV

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A B S T R A C T

Proton induced X-ray emission using a peltier cooled X-ray detector was used to determine the concentrations of 10 elements in 20 clay pottery samples collected from excavated Buddhist sites of four districts of Telangana and Andhra Pradesh states, India. The provenance (same or different origin) of pottery samples were determined soil samples from corresponding sites with known origin were analyzed for the validation of provenance methodology adopted in this study. For determining accuracy of the proton induced X-ray emission method, two certified reference materials namely SL-1 and soil-7 obtained from International Atomic energy Agency were analyzed. From these analyses, it was observed that both pottery and soil samples under study belong to four different groups.

K E Y W O R D S

Proton induced X-ray emission, Pottery, Peltier cooled detector, Soil samples.

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I N T R O D U C T I O N

Studies on archaeological artifacts constitute an important area of research to unravel the past human activities like art, culture and trade. Most of the studies focus on the provenance of the artifacts *i.e.*, whether they belong to same or different origin or group through the provenance studies. In the provenance studies, archaeological artifacts like pottery, bricks, stones, coins and paints are investigated [1-4]. Among these artifacts, potteries are most studied. Studies for provenance are carried out in two ways: either by classifying samples according to their physical characteristics, decoration and style or by chemical composition analysis [1,2]. Chemical composition analysis of artifacts is the most important tool for providing useful information like geographical origin and manufacturing techniques [3]. The chemical composition of a clay pottery is strongly related to the source of clay and recipe of the making [4]. It is known that the concentrations of major elements like Si, Al, Ca and Mg may not vary significantly compared to the elements present at trace levels [5]. The variation of trace elements depends on the place and preparation and hence determination of concentration of trace elements

becomes more important. Groups of elements used for the provenance studies are alkali and alkaline earth elements, transition elements and rare earth elements [3,6]. Elements which are non-volatile and immobile, exhibit high stability in clay minerals and therefore are good candidates for cluster analysis as any changes if found could be attributed to composition of making rather than due to migration, mobility and weathering with time [3,6]. The rare earth elements are used for provenance study due to their similar geochemical properties as well as highly insoluble and immobile nature. The alkali and alkaline earth elements like Na, K, Rb, Cs and Ba, have similar properties and expected to have correlation among them in clay and pottery samples. Correlations are also reported among the transition elements like Sc, Fe, Co, Cr, Hf and Mn, which are used for grouping of artifacts. For samples like pottery and bricks, making process involves high temperature treatment of wet/sun-drenched samples through firing. Therefore, ratios of concentrations of non-volatile elements like Al and Sc or elements having similar geochemical properties like La and Ce are used in the provenance studies of samples like potteries [1,7].

Elemental composition analysis of artifacts demands reliable results of concentrations at major to trace levels using a sensitive analytical method. Non-destructive nuclear analytical methods like neutron activation analysis (NAA), X-ray fluorescence (XRF) and particle induced X-ray emission (PIXE) have been used for the analysis of archaeological artifacts like potteries [7-14]. These methods have been applied to different samples with varying degrees of success in terms of sensitivity and multielement capability.

E X P E R I M E N T A L

Sample collection sites: Although archaeologists so far have identified more than 140 Buddhist sites in Telangana and Andhra Pradesh, ranging in date from pre-Ashoka (250 century BC) to Vishnukundin times (424-620 century AD), stretching from Dantapuram in the North to Nandalur in the South and Kotilingala in the West to Bhattiprolu in the East of Andhra Pradesh, India [17], initially only seven important sites were selected. These are excavated Buddhist sites along the sea coast of Visakhapatnam, Srikakulam and other nearby places of Andhra Pradesh, India. The names of places and their geological coordinates are given in Table-1.

Collection of samples: The samples were collected under the supervision of personnel from the Department of Archaeology and Museums, Government of Andhra Pradesh, India. Pottery samples of different shapes, with length of 6-15

cm weighing about 250 g to 1 kg were collected from the above sites. Pottery samples were washed off sticking soil, if any, with water, wiped with soft cloth and sealed in a clean polythene bag with a label. To examine the possibility of correlation of pottery results with soil or clay, sub surface soil samples (about 1 kg) were collected from a depth of about 10 cm. Soil samples were sun drenched; pebbles were removed and then sealed in clean polythene bags.

Sample preparation: The samples were powdered using agate pestle and mortar. The samples were dried at 105 °C in a hot air oven for about 24 h to remove any moisture content. Sample masses used were in the range of 75-150 mg. Sample mass of 400 mg was mixed with cellulose (binder) in 1:1 ratio along with yttrium oxide (1200 ppm of Y). The purpose of mixing yttrium oxide powder is to monitor the variation of beam current during irradiation. The resultant mixture was compressed using a 2 ton hydraulic press into pellets of 20 mm diameter and about 1 mm thickness. The International Atomic Energy Agency (IAEA) certified reference material (CRM) SL-3 (lake sediment) was used as a multielement comparator. Samples along with the multielement comparator were irradiated in different batches. The control samples, CRMs SL-1 and soil-7 were prepared and irradiated along with multielement comparator in the similar way to that of samples.

A proton beam of 2.5 MeV energy (current about 10 nA) obtained from the FOTIA (Folded Tandem Ion Accelerator), BARC, Mumbai was optimized for internal PIXE [5]. Pellets were placed on an aluminum ladder in the PIXE chamber at 45° to the beam direction and X-rays were analyzed using a peltier cooled Si(Li) detector of resolution 180 eV at 5.9 keV X-ray of Mn. Fig. 1 gives a schematic diagram of PIXE.

R E S U L T S   A N D   D I S C U S S I O N

Fig. 2 give the PIXE spectra of a pottery sample. The results obtained for IAEA RM SL-1 PIXE methods are given in Table-1. Though concentrations of 22 elements were determined, for comparison purpose results of 15 elements (Na, K, Ca, Ti, V, Cr, Mn, Fe, Co, Zn, Rb, As, Ga, La and Ce) are given. Using PIXE, concentrations of seven elements namely K, Ca, Ti, V, Cr, Mn, Fe, Rb and Zr were determined. The results of PIXE are found to be in good agreement with the certified/information values. Though, we have analyzed many samples of potteries, results of 14 elements in one of the representative clay potteries analyzed by PIXE are given in Table-2. Proton induced X-ray emission is a good alternate multi-element technique for ceramic samples for medium

TABLE-1 NAME AND COORDINATES OF SITES CHOSEN FOR POTTERY AND SOIL SAMPLES						
S. No.	ID of pottery	ID of soil	Site	Location (Town/District)	Latitude	Longitude
1	P-1	S-1	Dantapuram	Srikakulam	18.15 N	84.14 E
2	P-2	S-2	Jagathipadu	Srikakulam	18.28 N	84.28 E
3	P-3	S-3	Pavuralakonda	Visakhapatnam	17.53 N	83.30 E
4	P-4	S-4	Thotlakonda	Visakhapatnam	17.15 N	83.23 E
5	P-5	S-5	Bavikonda	Visakhapatnam	17.14 N	83.25 E
6	P-6	S-6	Boppikonda	Tuni	17.21 N	82.35 E
7	P-7	S-7	Gullacholangi	Kakinada	16.57 N	82.15 E

6 mV folded Tanded ion accelerator facility
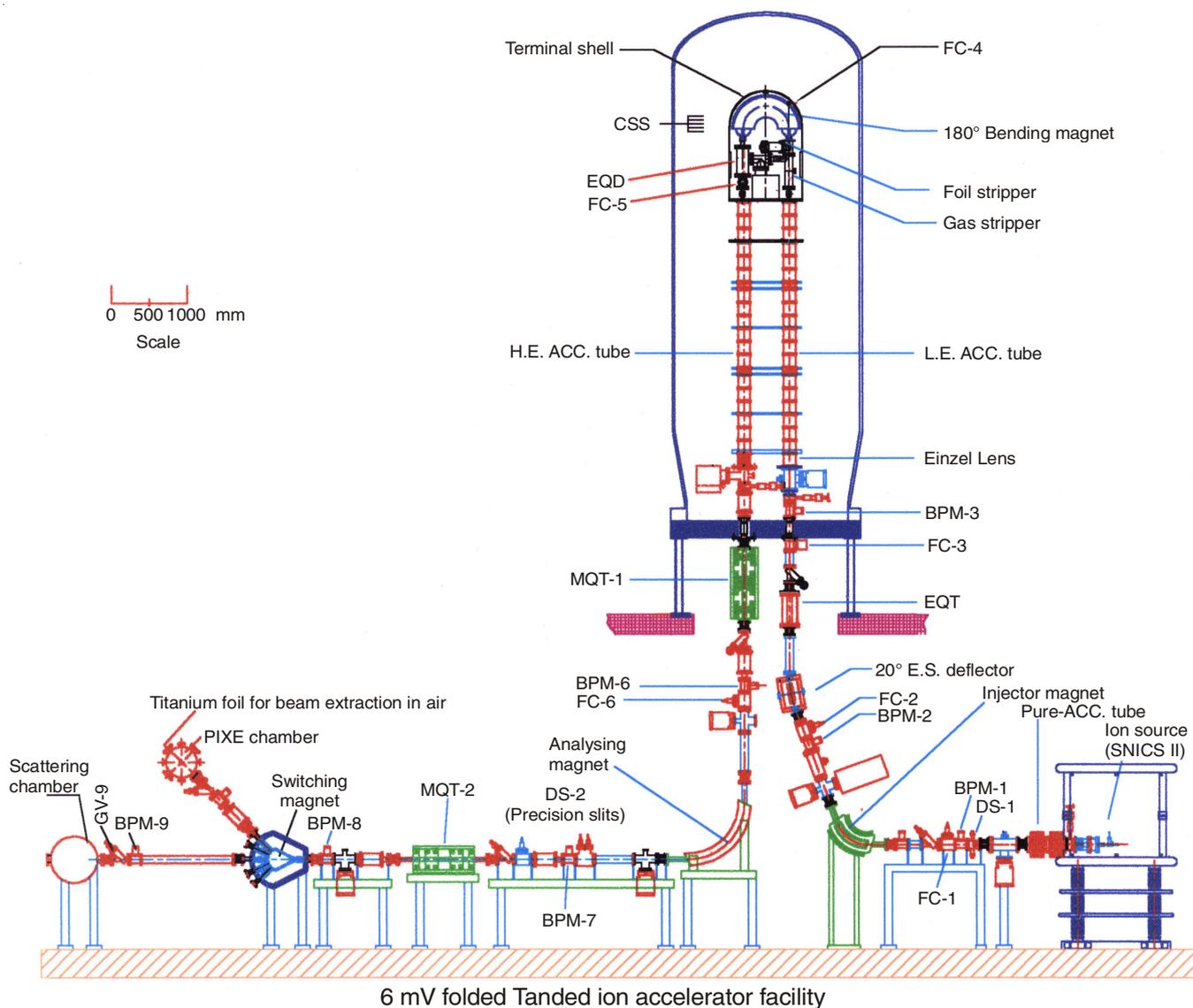
Fig. 1. Schematic diagram of PIXE
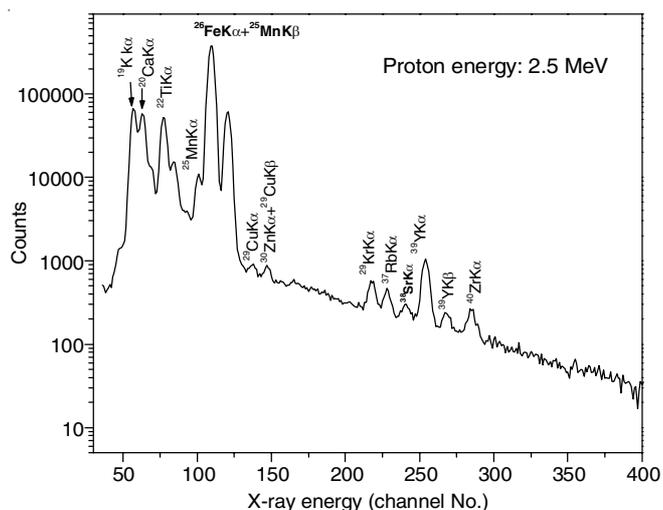
Fig. 2. PIXE X-ray spectrum of a pottery sample

TABLE-2
COMPARISON OF CONCENTRATIONS (ppm)
OF IAEA SL-1 BY PIXE

Elements	Certified values	PIXE
Na	1720 ± 120	Not detected
K	15000	15480 ± 461
Ca	(2500)	2595 ± 37
Ti	5170 ± 361	4800 ± 38
V	(170)	155 ± 6
Cr	(104)	95 ± 3
Mn	3460 ± 173	3448 ± 61
Fe	67400 ± 2022	65865 ± 164
Co	19.8 ± 1.5	Not detected
Zn	223 ± 9	Not detected
Rb	113 ± 11	124 ± 7
Zr	(241)	264 ± 12
As	(27.5)	Not detected
Ga	(24)	Not detected
Ce	(11.7)	Not detected
La	52.6 ±2.7	Not detected

Z elements. Further work on utilization of PIXE is being pursued using FOTIA and other accelerator facilities. The

concentrations of 20 elements were determined from four replicate experiments in all samples and certified reference

materials. The percentage deviations of the determined concentrations in IAEA CRMs SL-1 and soil-7 are within ± 8 %. The determined values were in good agreement with their certified or information values. Z-score values in these certified reference materials were found to be in the range of -2.0 to 1.8, which are found to be well below the accepted value of ± 3. Results of the elemental concentrations in soil and pottery samples are given in Table-2. Concentrations of major elements Al, Fe, Ti, K, Na, Mn and Ba are in the range of 8.0 to 0.03 % whereas other elements are in the mg kg^{-1} range.

Conclusion

Proton induced X-ray emission using a proton beam of 2.5 MeV from the 6 mV FOTIA accelerator and high resolution X-ray peltier cooled detector was used to determine concentrations of 20 elements of significance in ancient pottery samples. Our approach of establishing provenance or grouping through elemental composition in conjunction with cluster analysis could be used for arriving at the source though the number of samples is less. Proton induced X-ray emission is an ideal, non-destructive technique for studying the provenance of pottery samples. The study is being extended to more number of such samples collected from different such ancient places of Andhra Pradesh and its neighboring states.

REFERENCES

1. J.W. Beal and I. Olmez, *J. Radioanal. Nucl. Chem.*, **221**, 9 (1997); http://dx.doi.org/10.1007/BF02035235.

2. H.R. Tykot, in eds.: M. Milazzo and M. Piacentini, Proceedings of the International School of Physics, "Enrico Fermi" Course CLIV (2004).

3. F. Monroy-Guzman and P. Fournier, IAEA Technical Report Series No 416, International Atomic Energy Agency, Vienna, Chap. 9, p. 147 (2003).

4. IAEA Technical Report Series No 416, International Atomic Energy Agency, Vienna, Chap. 1, p. 3 (2003).

5. M. Balla, G. Keomley and G. Rosner, *J. Radioanal. Nucl. Chem.*, **141**, 7 (1990); http://dx.doi.org/10.1007/BF02060180.

6. I. Rossini, J.C. Abbe, B. Guevara and R. Tenorio, *J. Radioanal. Nucl. Chem.*, **170**, 411 (1993); http://dx.doi.org/10.1007/BF02041477.

7. D. Tenorio, M.G. Almazán-Torres, F. Monroy-Guzmán, N.L. Rodríguez-García and L.C. Longoria, *J. Radioanal. Nucl. Chem.*, **266**, 471 (2005); http://dx.doi.org/10.1007/s10967-005-0933-0.

8. W.D. James, R.L. Brewington and H.J. Shafer, *J. Radioanal. Nucl. Chem.*, **192**, 109 (1995); http://dx.doi.org/10.1007/BF02037743.

9. M. Roumie, P. Reynolds, C. Atallah, E. Bakraji, K. Zahraman and B. Nsouli, *Nucl. Instrum. Methods B*, **249**, 612 (2006); http://dx.doi.org/10.1016/j.nimb.2006.03.067.

10. E.H. Bakraji, *J. Radioanal. Nucl. Chem.*, **264**, 645 (2005); http://dx.doi.org/10.1007/s10967-005-0765-y.

11. K.T. Biro, *J. Radioanal. Nucl. Chem.*, **265**, 235 (2005); http://dx.doi.org/10.1007/s10967-005-0814-6.

12. E. Witkowska, K. Szczepaniak and M. Biziuk, *J. Radioanal. Nucl. Chem.*, **265**, 141 (2005); http://dx.doi.org/10.1007/s10967-005-0799-1.

13. C. Menninga, L. Minc, M.D. Glascock and C. Descantes, *J. Radioanal. Nucl. Chem.*, **266**, 235 (2005); http://dx.doi.org/10.1007/s10967-005-0898-z.

14. U.M. Vinagre Filho, R.M. Latini, A.V.B. Bellido, A. Buarque and A.M. Borges, *Braz. J. Phys.*, **35(3b)**, 779 (2005); http://dx.doi.org/10.1590/S0103-97332005000500015.