



Investigations on Megalithic Pottery Samples by X-ray Emission Spectroscopy (EDXRF and XANES)

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ABSTRACT: Megalithic pottery samples (Red ware-RW, Black Polished ware –BPW and Black Red ware BRW) were studied for their trace element compositions by EDXRF (Energy Dispersive X-ray Fluorescence) and later for the oxidation states by XANES (X-ray Absorption Near Edge Structure). It was found that elements Fe, Cu, Zn, Sr, Nb and Mo were predominantly present in the pottery samples using an EDXRF system consisting of radio-isotope Cd 109, a Si(Li) detector of resolution 170 eV at 5.9 keV and PCA. XANES spectra of Fe, Cu and Zn obtained from INDUS-2 Synchrotron Source showed different oxidation states. The Fe edge indicated mixed oxidation states of +2 and +3 for iron in all the samples. Zn is present in the elemental form in all the samples. In the case of Cuit was found that Cu is in 2+ oxidation state in case of RWI sample and the other two samples, oxidation states were in elemental form. The motive of the study was to obtain an insight into the cultural heritage of Megalithic pottery samples using X-ray Emission Spectroscopy.

Keywords: Megalithic, pottery, EDXRF, XANES, Red Ware, tracelements.

INTRODUCTION

Archaeology is the study of past societies through the material remains left by those societies and the evidence of their environment. Potteries are the most abundant findings among the archaeological artifacts. Pottery analysis reveals information regarding the daily life and cultural aspects of the society of the ancient period¹. The scientific investigation greatly contributes to archaeology by providing definite and undoubted data about materials, production techniques of potteries to solve the attributed questions. Chemical analysis and technical examination of potteries play an essential role in providing important historical and technical information to have further understanding of our cultural heritage notably in connection with the restoration, conservation, dating and authentication of artifacts. Potteries were made from clay as raw material. In addition the nature and quality of the potteries depends on the firing temperature, firing atmosphere and the technical skill of potters. The technical skills of the ancient potters have been the subject of active research for gaining a deep insight of forgone culture². By analyzing the mineral trapped in the sample one can elucidate its firing temperature^{3 & 4}. Using spectroscopic technique one can search back the composition and processing which were applied during production time

MATERIAL AND METHODS

Three Megalithic sites excavated at Khanapuram Haveli which is located in the Khammam, between northern latitude 17°15'19"N deg, and eastern longitude 80°9'46"E deg, Andhra Pradesh, India. An archaeological excavation was performed under the superintendence of Department of History, University of Hyderabad and Department of History, SR&BGNR Govt. Arts & Science College, Khammam, Andhra

Pradesh in May 2012. Numerous shreds of potteries and ceramics with different size and style were recovered from site 1 and site 3 in trenches of dimension 3 by 3 meter and depth of 1.8 m and 4 by 4 meter and depth of 2.4m from the surface of the site location respectively. The artifacts recovered were treated conventionally for removing the dirt and stain and categorized. Few samples were selected at random for the present study.



Fig 1: Excavated Megalithic sites where the pottery shreds were collected.

VISUAL CHARACTERISTICS OF SAMPLES:

Sample 1: Outer surface of the sample is red in color and inner side of the sample is gray in color the sample sand witching portion is black in color.



Sample 2: Outer surface of the sample is fine red(polished red) in color and inner side of the sample is pale red in color, the sample sand witching portion is black in color in core area with red side walls.



Sample 3: Outer surface of the sample is black and red in color and inner side of the sample is black in color the sample sand witching portion is also black in color.



EDXRF: The samples were powdered and a qualitative run was carried out using the experimental set-up of EDXRF consisting of a Si (Li) detector cooled at liquid nitrogen temperature (77^0K), an amplifier and PC based MCA.

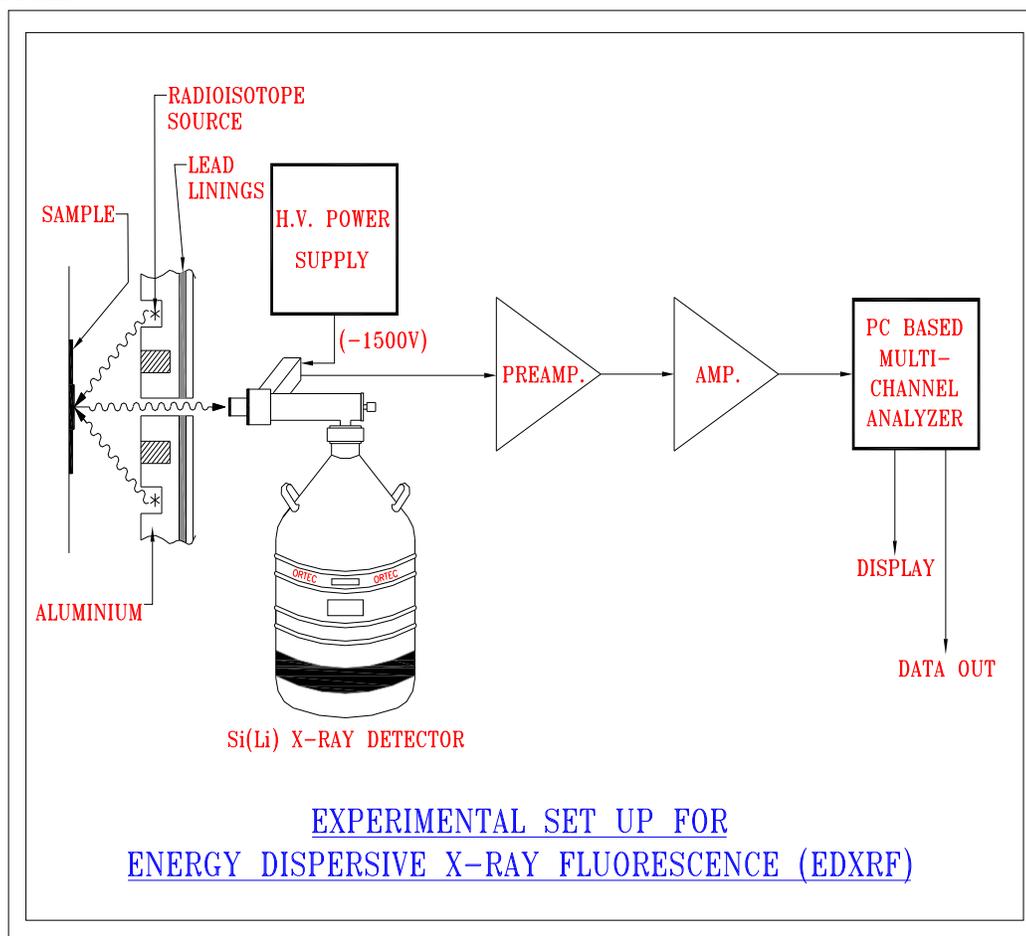


Figure 2: Experimental set up of EDXRF.

A reverse bias of 800 V was applied across the semiconductor junction of Si (Li) detector and the resolution of the detector was 170 eV at 5.9 keV. The sample was placed in front of an XRF spectrometer. For the excitation of the samples, Cd^{109} radioactive source was employed in annular geometry to prevent the direct exposure of the excitation source to the detector and minimize backscatter interference. The Cd^{109} emits Ag K X-rays (energy 22.25 keV). The X-ray spectra were recorded for a counting time of 2000 seconds and stored in a PC based multi-channel analyzer for further offline analysis. The Figure 3 gives the X-ray spectrum of RW-I .Figure 4 gives the X-ray spectrum of Red Polished ware.

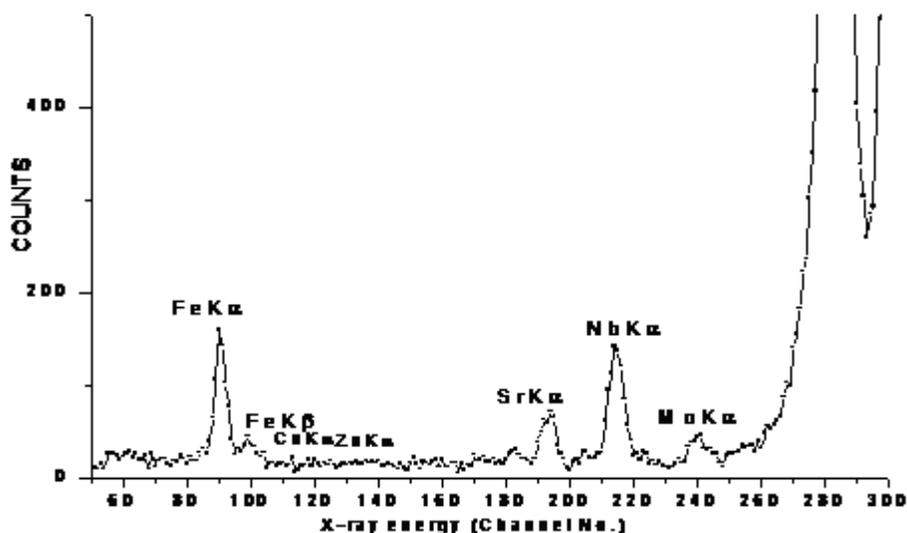


Figure 3: X-ray spectrum of RW II (Red Polished Ware)

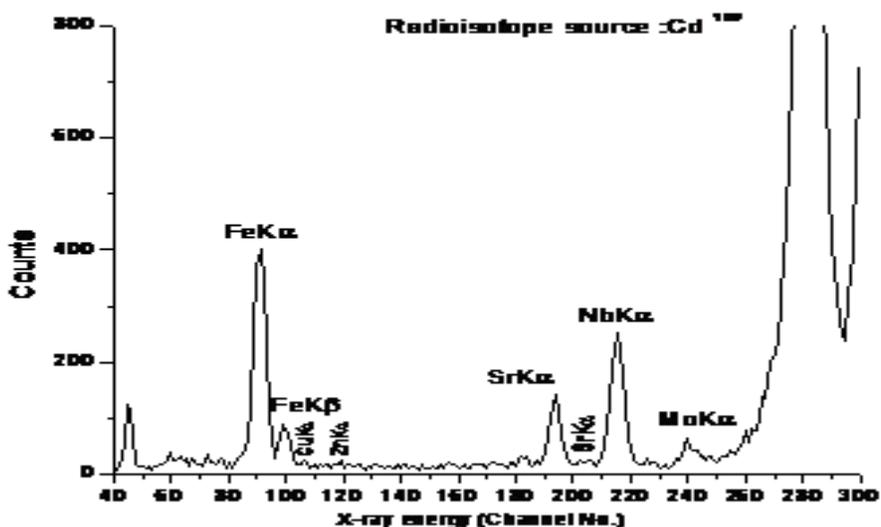


Figure 4: X-ray spectrum of RW-I (Red Ware-I)

XANES: XANES measurements were carried out on pottery (powder) samples. The XANES measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the INDUS-2 Synchrotron Source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India^{5&6}. This beamline operates in energy range of 4 KeV to 25 KeV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si(111) (2d=6.2709) based double crystal monochromator. The second crystal of DCM is a sagittal cylinder used for horizontal focusing. An ionization chamber (300 mm length each) is used to measure the incident x-ray intensity and a silicon drift detector is used for measuring fluorescence intensity coming out from the sample at a 45° geometry. The ratio of fluorescence count to the incident intensity as measured by the ionization chamber gives the measure of absorption coefficient (μ) at a particular energy selected by the DCM setting and the whole EXAFS spectrum is obtained by scanning the DCM over the whole energy range of interest. Homogenous pellets of 15 mm diameter have been prepared using an electrically operated hydraulic press.

RESULTS AND DISCUSSION

The normalized XANES spectra at Fe K-edge for all the samples are plotted in figure 5 along with Fe metal foil, and that of standard commercial powders of FeO, Fe₃O₄ and Fe₂O₃ where Fe has oxidation state of +2, mixed oxidation state of +2 & +3 and +3 respectively. The pre-edge features in oxides below the main edge are due to Fe 1s transition into unoccupied O 2p-Fe 3d (or Fe 3d/4p) hybridized states, which have p components projected at the Fe site as observed in many transition-metal oxides. The main feature at the Fe K-edge corresponds to the high-energy Fe 4p states. The edge position in all the samples is obtained from maxima of first derivative of normalized XANES spectra. The edge position of all three samples is at the same position (7123 eV) as for Fe₃O₄ and far away from FeO (7119) and Fe₂O₃ (7126.5eV) which indicated mixed oxidation states of +2 and +3 for iron in all the samples.

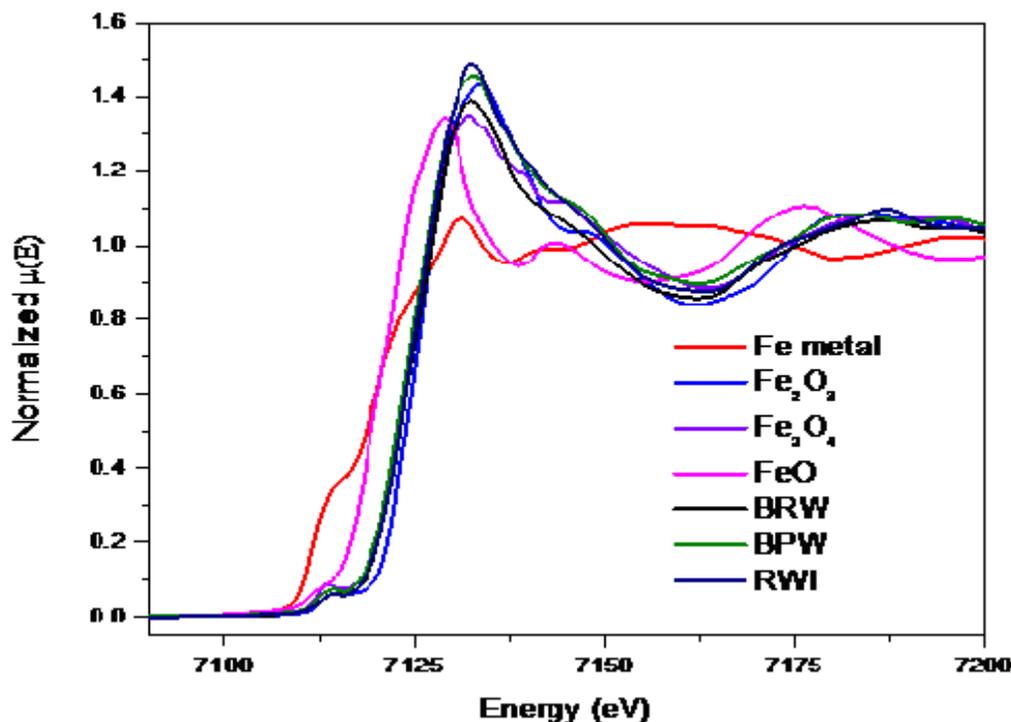


Figure 5: Normalised XANES spectra of pottery samples at Fe K-edge

The normalized XANES spectra of all the three samples at Zn K edge are shown in figure 6 along with that of Zn metal foil. Since the absorption edges of Zn in all the three samples coincide with that of Zn metal foil, it suggests that Zn is present in the elemental form in all the samples.

The XANES spectra for Cu K edge is shown in Figure 7 along with Cu metal foil standard. Maximum of first derivative is taken as edge position in all the samples. The XANES spectra of Cu metal shows two K1 and K2 edge. The maximum of first derivative of Cu metal K1 edge is found to be at 8979 eV and that of K2 edge is at 8990 eV. In case of RPW and BRW samples also the maxima of first derivative of K1 edge is found to be at 8979 eV and that of K2 edge is at 8989.5 eV. Since both K1 and K2 edge maxima are at the same position as in Cu metal foil only the relative amplitude has been changed, we can conclude that Cu in both RPW and BRW samples are in elemental Cu state. On the other hand, in case of RWI sample the maxima of first derivative at 8985 eV and edge features are quite different from the other two samples. The edge position suggests that Cu is in 2+ oxidation state in case of RWI sample.

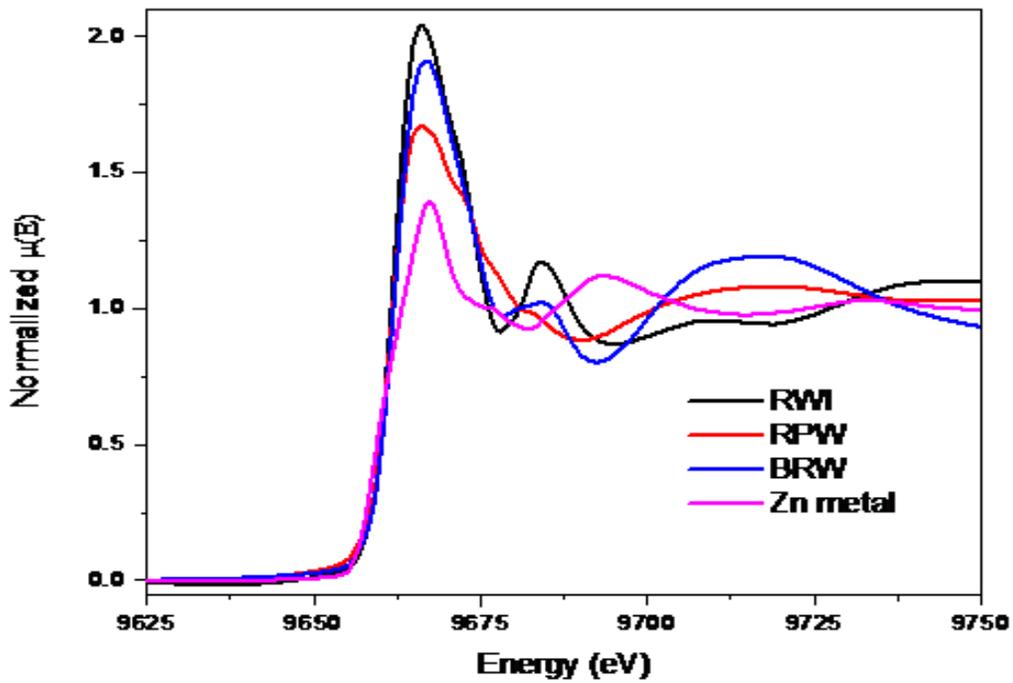


Figure 6: Normalised XANES spectra of pottery samples at Zn K-edge

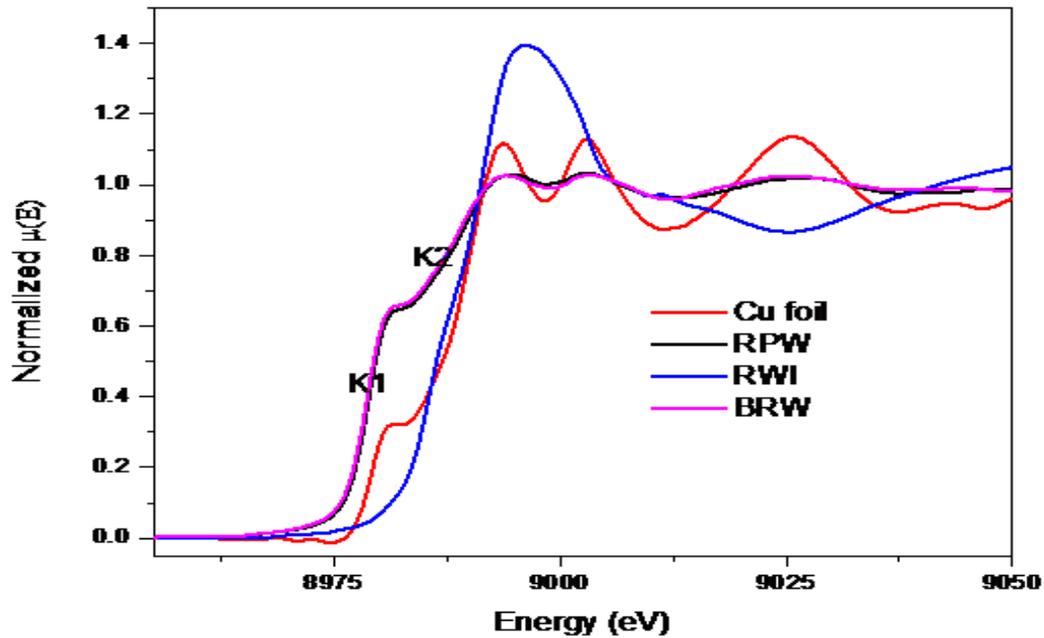


Figure 7: Normalised XANES spectra of pottery samples at Cu K-edge

CONCLUSION

EDXRF studies showed that a large amount of Fe is present in all samples and they exist in a mixture of oxidation states of +2 and +3, which leads to their reddish, blackish color. The other significant element present is Sr and Nb . XANES spectra of Zn showed Zn present in elemental form and Cu is present in

+2 state in Red ware indicating the red color To a certain extent the cultural practice can be inferred by investigating the mineralogical characteristics of the Megalithic pottery samples. It is concluded that X-ray Emission studies can be helpful in obtaining trace element characterization of Megalithic pottery samples and their significance.

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