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FTIR AND XRD STUDIES ON SOME ARCHAEOLOGICAL ARTIFACTS FROM BOHN, INDIA

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Abstract

Spectroscopic studies have been performed on archaeological pottery samples from Bhon in Maharashtra. The clay mineral type and its structural deformation due to firing have been studied from their Fourier Transform Infrared (FTIR) spectra. The maximum firing temperature attained during baking, firing conditions (open/reduced atmosphere) and iron mineral phase changes are well established. X-ray diffraction (XRD) studies on archaeological artifacts pave the way to identify the minerals.

Key Words: Archaeological Pottery; FTIR; XRD.

Introduction

The technical and artistic quality of archaeological ceramics are important indicators for the achievements of prehistoric societies. Pottery samples are one of the few vestiges of the prehistoric past that provide some archaeological information about the country's first inhabitants. Archaeological studies are concerned with discovery through explorations and excavations, interpretations of material discovered, thereby understanding its significance which are relevant to the human development and conservation of the objects excavated (Gurumurthy, 1981). Clay, the chief ingredient used in pottery, is a fine grained material that develops some ductile behavior when mixed with water. The main components of clay are Si, Al and water which also contains small amounts of feldspars, biotite, carbonates, Fe-Ti oxides as well as soluble salts and organic matter. The most common Fe minerals in clays especially important in archaeomagnetic studies are hematite, goethite, limonite, magnetite and siderite (Rodriguez et al., 1999). The making of pottery involves different steps (shepard, 1963) collection and preparation of the clay, modeling of the artifacts, surface finishing, decoration, drying and hardening by heat. Clay firing is one of the earliest technological operations of mankind. Clay firing, if properly conducted with respect to material and process, produces exceedingly durable artifacts. Scientific studies are used to explore the technological development of the prehistoric man. The clay intended for making vessels is devoid of impurities and possesses fine plasticity, the vessels made out of it will be of a better quality.

The clay minerals as well as associated minerals including iron oxides undergo characteristic chemical and physical changes during firing which can be followed by different techniques like X-ray diffraction, Scanning Electron Microscope, Differential Thermal Analysis, Optical Microscopy, Mössbauer Studies, FTIR, etc. Of the various well known methods of analysis, infrared absorption spectroscopy is a rapid, economical and non destructive physical method universally applicable for structural analysis of clay minerals. Infrared spectroscopy is a sensitive technique to monitor dyhydroxylation and dehydration of clay minerals (Russel, 1987). On firing the clay materials the structural deformation of the clay minerals and associated minerals depend upon firing temperature and atmosphere, which can be followed by FTIR. (Venkatachalapathy et al., 2002, 2003; Murad and Wagner, 1994). Knowledge of the firing temperature can be of value in other scientific investigations of ancient ceramics and kilns.

The effect of X-ray diffraction by mineral structure constitutes the basis for identifying minerals and other crystalline substances. The diffraction of X-ray is of great analytical significance, as every crystalline substance would scatter to the X-rays in its own unique diffraction pattern, giving finger print of its atomic arrangement. Berry (1974) has carried out an extensive work on all types of minerals and reported a file called selected powder diffraction data for mineralogy (Joint Committee on Powder Diffraction Standards). For the present study the archaeological pottery samples collected from Bhon (Bon) [Lat. 76°39'E; Long.20°55'N] samples were subjected to FTIR and XRD studies in order to reveal the firing temperature, firing conditions and minerals identification.

Site location and experimental details

Bhon (BON) [Lat. 76°39'E; Long.20°55'N] is situated at Sargrampour Taluk of Buldana District, Maharashtra, India and the excavations have been carried out by Deccan College, Pune, India. Representative samples from different trenches at various depth were used for the present study.

The FTIR absorption spectra were recorded in the frequency region 4000-400 cm^{-1}, using model paragon 500, Perkin-Elmer spectrophotometer with 16 scan mode by using standard KBr pellet technique. The accuracy of the measurement is $\pm$ 4cm^{-1} in 4000 to 2000 cm^{-1} region and $\pm$ 2 cm^{-1} in 2000 to 400 cm^{-1} region. The X-ray powder diffraction spectra pattern has been recorded on X´pert MPD from Philips using Cuk_α radiation at a wavelength of 1.54050Å and the 2θ range from 20° to 70° in steps of 0.0200Å and counting time 0.30 per step.

Results and Discussion

Infrared spectroscopy has been for decades, a frequently used method to investigate the structure, bonding and chemical properties of clay minerals. On firing the pottery clay to higher temperature in order to get the final products, thermal changes are taking place mainly on structure and bonding of clay minerals, which can be studied by using FTIR studies. Similar observations on clay minerals and their transformation during firing on fired pottery samples have been elaborately studied by many authors (Farmer, et al., 2000; Russel, 1987; Madajova, 2003; Murad, et al., 1998; Venkatachalapathy, et al., 2002; Manoharan, et al., 2007) using FTIR.

In the present study the room temperature FTIR absorption spectra of pottery sherds BON-1, 8, 15 and 62 in the as received state are shown in Fig.1. The absence of the bands at 3700 cm^{-1} and 3620cm^{-1} which are assigned to O-H stretching of inter layer water and inner O-H group of absorbed water, indicates that the samples have been fired above 450 °C. The destruction of inner O-H structure completes around 450°C (Venkatachalapathy, 2002). The presence of the bands at 3450 and 1640 cm^{-1} in the as received state are attributed to O-H stretching and H-O-H bending vibration of adsorbed water molecules. During refiring of the sherds, the above bands get diminished and disappeared at 500°C, indicating the complete evaporation of water molecules (Venkatachalapathy, 2003). The presence of the bands at 1100, 935 and 915 cm^{-1} and the presence of a broad symmetry band at 1030 cm^{-1} are assigned to [$Al-O-(OH)_6$], O-H deformation. Al-OH and Si-O-Si respectively. Usually when firing the clay materials between 200 to 600°C, the expandable layer silicate collapses, resulting in the disappearance of the bands at 1100, 935 along with 915 cm^{-1} and appearance of a broad symmetry band at 1030 cm^{-1} for red clay and 1080 cm^{-1} for white clay (Ghosh, 1978).

The presence of the bands at 795, 775 along with 695 cm^{-1} is due to quartz (Ojima, 2003). Quartz and feldspar are often present in clays either they are present already in the clay, or added as temper. The weak band at 640 cm^{-1} is attributed to Al-O co-ordination vibration. The intensity of the band 530 cm^{-1} decreases above 400°C and is shifted to 540 cm^{-1} due to the replacement of Al by Fe (Maniatis et al., 1981). The band 540 cm^{-1} along with the appearance of weak shoulder at 580 cm^{-1} are attributed to iron oxides at 500°C. The increase in intensity of the above band beyond 600°C indicates the crystallization of hematite. The absence of hydroxyl bands and the presence of broad symmetry band centered around 1030 cm^{-1} in the as-received state spectra indicate that all the samples have been fired above 600°C and are made up of disordered clay. The presence of bands at 1440 and 875 cm^{-1} are attributed to calcite (Ghosh, 1978), which persists upto 700°C and disappears at 800°C. The above result is in agreement with the report of Maniatis and Tite (1978) that calcite dissociates in the firing temperatures between 600 and 750°C. The well resolved and distinct peaks at 540 and 580 cm^{-1} in the spectra of as received state in all samples reveals the presence of iron oxides, which also confirms the firing temperature as above 600°C. The well resolved distinct peak observed at 540 and 580 cm^{-1} in the case of samples BON-1, 15 and 62 indicates that the samples are fired under reduced atmosphere and the kiln might have been opened at a higher temperature (or) fired under oxidizing atmosphere. The distinct peaks at 540 and 580 cm^{-1} with weak intensity in the case of samples BON-8 indicate that the samples were fired under reduced atmosphere or kiln was opened at low temperature followed by reduced atmosphere. Samples fired under strong reduced atmosphere will result in the black ware.

XRD Analysis

X-ray Powder Diffraction (XRD) is an extremely useful tool for mineralogical analysis. The identification of the structure of a clay mineral is best accomplished by X-ray analysis. To identify the mineralogy in archaeological potteries, XRD spectra pattern have been recorded in the 2θ range from 20° to 70° for the representative samples. The minerals have been identified from the peak positions of the spectra using JCPDS file.

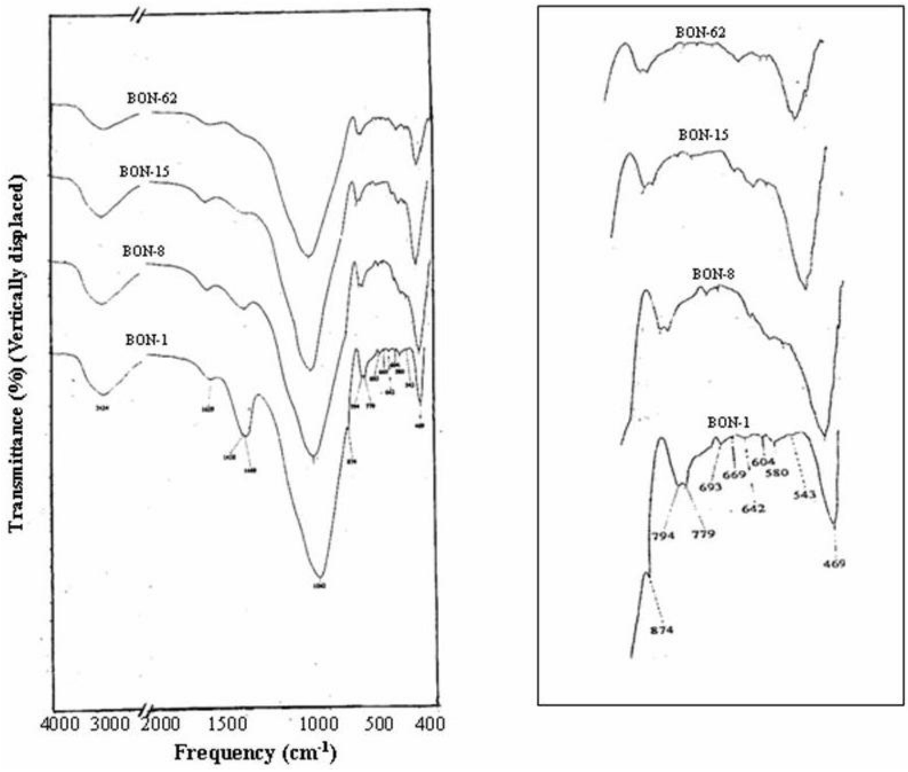

Fig.1. FTIR Absorption spectra of Bhon potteries in as-received state

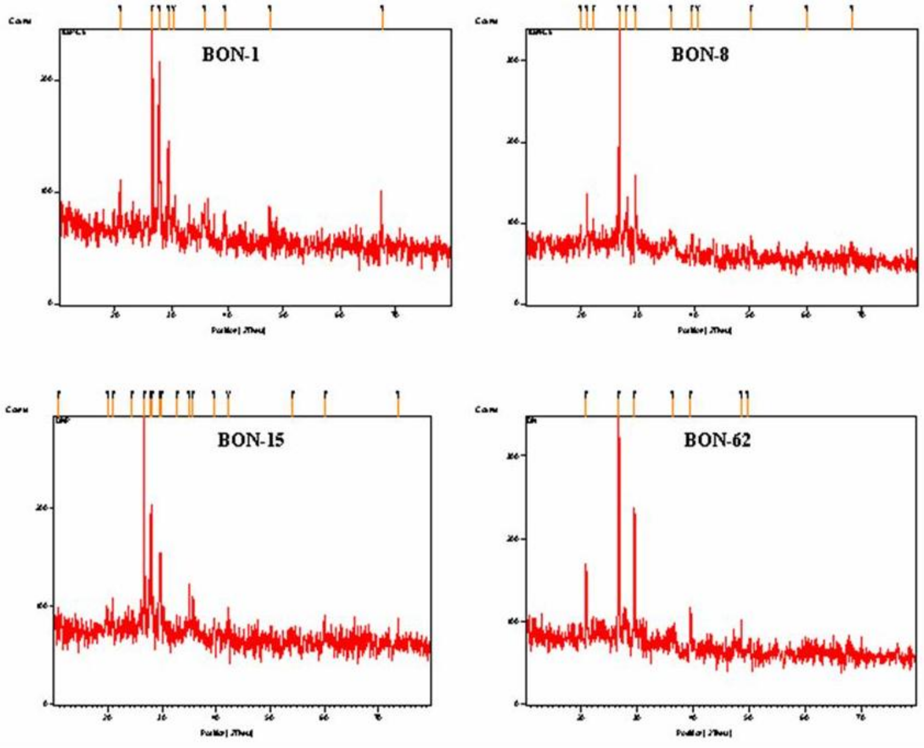

Fig.2. X-Ray Diffraction spectra of Bhon potteries in as-received state

For the present investigation, the XRD spectra have been recorded at room temperature for the samples BON-1, 8, 15 and 62 are shown in Fig.2. The minerals associated with the samples are identified using JCPDS file (JCPDS, 1999) While identifying the minerals only prominent peaks of the respective minerals are considered, the peaks, which overlap with other minerals are omitted for analysis. In BON-1, the identified minerals are quartz (4.25574, 3.34895 and 2.28209Å), albite (3.20249Å), calcite (3.03161Å) hematite (2.94134Å) and magnetite (2.53033Å) while in BON-8, the identified minerals are quartz (4.23526, 3.33283Å), anorthite (3.01898Å), hematite (2.2864Å) and magnetite (2.52421Å). In BON-15, the identified minerals are quartz (4.24337, 3.33748, 2.27574 and 1.53675Å), calcite (3.01463Å), oligoclase (3.63801, 3.17509Å) and hematite (2.51380Å). The minerals identified in BON-62 are quartz (4.24892, 3.34047 and 2.47257Å), calcite (3.02768Å), orthoclase (3.7450Å) and hematite (1.83369Å). From the XRD pattern of the samples, the minerals quartz, anorthite, albite, hematite and magnetite are identified. Quartz is predominant and makes clay self tempered.

Conclusion

Lower limit of firing temperature for the archaeological artifacts are well established from the bands around 3695, 3620, 1100, 1030, 915 and 530 cm^{-1}, which are sensitive to temperature effects, and found that most of the samples are fired above 600°C. The presence of iron oxides in artifacts was established from the absorption bands 540 and 580 cm^{-1}. The different firing atmosphere / temperature established through FTIR studies reveals the artisans awareness and skill in manufacturing different coloured / varieties of pottery for different utilities and for trading. The presence of calcium is rich (peak at 1440 and 875cm^{-1} are intense) in the case of the samples in the depth 0-36cm^{-1}.

Major minerals like quartz, calcite, albite and orthoclase, and iron oxides have been identified from the XRD spectra.

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