

X-RAY DIFFRACTION STUDIES OF ANCIENT INDIAN GLAZED WARE

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Abstract:

Northern Black Polished Ware is subject of enquiry in this paper. This is an important pottery tradition of the Ganga Valley. This ware has a very high lustrous finish and shows variations in colour. There are many problems related to its origin, distribution and technology of manufacturing. In this paper an attempt has been made, using X-ray diffraction techniques, to address the problems related to its firing technology. It is being proposed that NBPW production was distributed over a wider area of the Ganga Valley and it was a specialized craft in ancient India. It has been found that due to special technique of firing the clay minerals present on the outer surface of pottery underwent mineral transformation and produced a lustrous glossy slip.

Key Words: Indian Subcontinent, Kausambi, NBPW, XRD, Glaze

Introduction

Kausambi is one of the oldest cities of the early historic India, which is closely associated with the legends of the Buddha (6th-5th c. BC). Archaeologically it can be termed as a key site of the Gangetic plane (Rai 2010), which has a wide range of cultural relics. Other important sites, within a buffer zone of 30km from Kausambi, are Bhita and Sringerapuram (Fig. 1).



Figure 1: Map showing archaeological site of Kausambi and other important sites in Ganga Valley

The antiquities recovered from this site make it a very important site (Sharma, 1960, 1969, 1980). There are four localities where excavation was conducted: Ghoshitarama monastery area, Asokan Pillar

area, Defence area and The Palace area. Terracotta art and different types of pottery have been recovered from all the four localities. The earliest evidence of NBPW comes from this site at the level of 600 BC. NBPW has been reported at the level of 600 BC from this site (Sharma 1960). NBPW was first noticed in the excavation at Saranath (Varanasi) in 1904 and then in Bhita near Allahabad (Marshall 1915). At that time excavator could not distinguished it as a separate pottery tradition. During the excavation of Taxila, excavators found this pottery, and then they proposed that it is Greek Black Pottery. Till date this pottery has been reported from more than six hundred sites in the Indian subcontinent. It is found over a wide area; Chandraketugarh in east, Prabhaspatan in west, Udeygram & Charsadda in north and Amarawati in southern most. Its concentration in Ganga Valley (Northern India) is remarkable and that is why it is called “Northern” black polished ware. It is not entirely black and is found in many colours as grey, golden, orange-pink, chocolate, mercury etc. but most of the sherds are black. Its surface is very shining so it has a sobriquet Northern Black Polished Ware (Rai et al. 2014).

The origin and development of NBPW is ambiguous. When it was reported from Taxila, scholars thought that either it is Greek black pottery or it is a separate pottery tradition which has impact of Greek black pottery. When it was reported from earlier strata than Greek black pottery level, it confirmed that it is separate and unique pottery tradition and it is older than Greek black pottery. NBPW are deluxe ware associated with mainly table ware. It was related with aristocratic class. This pottery has been divided into five categories on the basis of its fabric. First type of pottery is of fine matrix & thin section with brilliant shine on the outer surfaces. Generally corrugated bowl come under this type. Second class of pottery is of thicker section and its surface is scratchable. Its gloss is less than that of the first type. Dishes and bowls come under this type. Third type of pottery has core of red to grey in colour and red, orange or yellow layer found under glossy surface. Fourth class of pottery is generally black and red ware and was perhaps a result of inverted firing technique. The fifth class of pottery is thick in section and surface is black and shining surface is absent or very low (Roy, 1983).

XRD examination of NBPW

X-Ray diffraction study of NBPW was carried out in order to get information about mineral geochemistry and crystalline status of pot-sherds. This investigation was done by Rigaku made diffractometer with Bragg-Brantano geometry (Cockcroft and Fitch 2008). It is a powder diffractometer in which fine grained samples are used. A total of five samples were investigated by XRD and the data were taken at the 2θ range of 10° - 80° . The XRD profile was analysed by Rietveld Method in order to get quantitative information (Von Dreele 2008) for the mineral phases present in samples. In Rietveld Method the whole pattern of the XRD profile is studied instead of the single peak. The Rietveld method has potential to produce more accurate and precise results than those obtained from conventional single peak

methods (Madsen and Scarlett 2008). The Quanto software (Altomare et al 2001) obtained from Institute of Crystallography has been used for Rietveld refinement.

A total of ten mineral phases were examined in pottery sample and seven mineral phases in brick sample. The main objective of refinement was to get quantitative information about mineral Kaolinite and Mullite. In the process of firing, Kaolinite changes in to Metakaoline and than in Mullite (Murray 2007: 75). This behavior is important in the investigation of firing temperature of pottery.

XRD Study and Minerals transformation

The examination of crystal structure by XRD throw light on firing process of NBPW. The phase purity of the NBPW samples was investigated by XRD; as a result four major and six minor phases were obtained. The XRD data of brick sample show different phase compositions but same elemental composition (Table 1 and 2). The major phase present in NBPW samples are Kaolinite, Biotite, Albite, and Mullite. On the other hand, Gibbsite, Kaolinite and Mullite are major phases present in the Brick sample.

Table 1. Ritveld analysis of the XRD data of Brick Sample

Sr. No.	Phase	% weight
1	Albite	8.991
2	Anorthite	1.144
3	Biotite	0.129
4	Gibbsite	20.118
5	Hydroxya	1.243
6	Kaolinite	60.878
7	Mullite	7.496

Table 2. Ritveld analysis of the XRD data of NBPW sample

Sr. No.	Phase	% weight
1	Albite	15.090
2	Anatase	1.926
3	Anorthite	1.936
4	Biotite	15.103
5	Ca-Oxide	0.173
6	Calcite	0.078
7	Gibbsite	2.190
8	Hydroxya	0.133

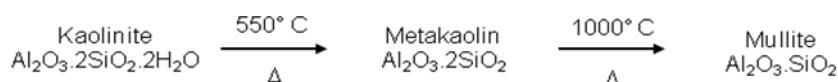
9	Kaolinite	16.797
10	Mullite	46.574

Since the manufacturing of bricks is carried out at a considerably low temperature for maintaining porosity, the mineral transformation occurs rarely. But in the case of glazed pottery production, high temperature is maintained in order to achieve hard and vitrified pottery surface.

The XRD data show that Kaolinite is $\approx 60\%$ w and Mullite is $\approx 7\%$ w. This suggests that Kaolinite is the major mineral of the ancient clay in this region.

Estimation of Firing Temperature and Role of Minerals in glaze formation:

Ceramic glazes are glassy substance formed by melting of earthy materials and transformation of crypto-crystalline earthy material into non-crystalline substance. It has three components – network formers, network modifiers and intermediates (for details see Rice 1987: 99). When clay is fired, it undergoes some chemical changes and it acquires many of the qualities that make clay into pottery. The heat supplied during the firing process provides sufficient energy to dislodge atoms from their positions within the clay and cause them to migrate to more favorable sites. The final result of the firing process is that the clay is converted to a new hard and rigid ceramic material that is stable to water, high temperatures, and weathering (Goffer 2007: 237, Polard and Heron 2008: 98). When temperature exceeds more than 700 °C clay minerals undergo tremendous changes in which some minerals completely fuse their micro-structure and transform into new minerals phase. The phase change at 980 °C transform Kaolinite into Mullite phase and at continuous temperature around 1000 °C completely transform Kaolinite.



XRD result shows that the brick sample has high percentage of Kaolinite and low percentage of Mullite phase. The bricks were fired at low temperature so the transformation of Kaolinite into Mullite had not been completely occurred but in case of pot sherds, The concentration of Mullite is much more than Kaolinite. It suggests that pottery was been fired at temperature around 1000 °C but temperature did not exceed more than 1000 °C that is why complete transformation of Kaolinite into Mullite did not occur. For the glaze it can be said that it is not any kind of slip, but it has been formed during firing process and minerals transformation due to thermolysis is responsible for glaze.

Conclusions

This study shows that NBPW production was not confined to a particular area, but was distributed across the whole Gangetic plain, if not beyond. The ancient potters were using locally available clay to

manufacture this special kind of pottery (Rai et al. 2016) and the technology of production was a very sophisticated one. The knowledge of manufacturing technology was restricted to special groups of potters, but disappeared with the passage of time. XRD results show that considerable amount of minerals have been fused to form Mullite during the firing process of pottery. It is very much possible that the glaze formation occurred due to mineral pyrolysis. The application of extra layer of clay or any other material is difficult to explain. The most probable cause of glossy layer is mineral transformation due to high temperature.

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