Geochemical studies of the ancient Indian glazed ware

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The ancient Indian glazed pottery, which is often termed as northern black polished ware (NBPW), has a high lustrous finishing and it is closely related to the second urbanization in the Indian subcontinent. In this communication, an attempt has been made to review previous research related to manufacturing technology, especially the surface gloss and firing process, using SEM and EDS techniques. The objective of this communication is to address some of the problems relating to technological competence thus achieved at that point of time. NBPW was a specialized craft in ancient India, the competence of which gradually evolved.

Keywords: Geochemical studies, glazed finish, northern black polished ware, technological competence.

GEOCHEMICAL characterization of archaeological pottery constitutes a major role in understanding the manufacturing techniques of pottery. Due to the lack of any scientific basis for improvization in pottery construction techniques, a slow trial and error process in achieving the technological competence was prevalent within an ancient society. In the Indian subcontinent traces of glazing on ceramics can be pushed back till the Harappan period. Although the distinctive pottery of Harappan civilization is Harappan red ware[1], reserved glazed pottery[2] is also reported from Harappan sites.

Closed firing pits were a major technological innovation in the history of earthenware manufacturing. The closed kiln facilitates control over firing conditions to achieve reducing and oxidizing environment and the maximum utilization of temperature. In ancient societies glaze formation was of two main types, lead glazing and tin glazing[3]. This technique was in use in pre-medieval and medieval India in slightly different form where blend of soda, silica and lime was applied homogeneously on the pottery in the presence of oil. Metallic oxides were added to obtain different colours in glazed finish. After firing at high temperature the resulting mixture fused with the outer layer of the pottery resulting in smooth and shining slip[4] and thus this pottery became porcelain[5].

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A different type of technique was also applied on the pottery to create glaze. It was the result of a combination of CaO and wood ash as flux and due to high temperature, natural kiln gloss was created[3]. Thus glazing, as a specialized craft was in use at least during the 15th century BC, if not earlier. Northern black polished ware (NBPW) is one of the earliest glazed ware of the Indian subcontinent. The radiometric dates push its antiquity to 8th century BC, but it is generally associated with the archaeological sites of urban character developed during the Buddhist period (6th century BC onwards)[6,7]. There are many problems associated with NBPW. The validity of the nomenclature of NBPW, still in popular use, is questionable on three grounds. First, although the dominant type is black, it is found in several distinctive colours. Second, the geographical expansion of this pottery type is not limited to northern India, but covers almost the whole Indian subcontinent. The origin and development of NBPW is not clearly known. The aim of this communication is to provide an insight into manufacturing technology, especially the surface gloss and firing process, by reviewing the reported processes in previous researches and comparing and contrasting the techniques such as SEM and EDS.

When this class of pottery was reported from Taxila[8,9], researchers thought that it was either Greek black pottery or a separate pottery tradition greatly influenced by Greek black pottery. Further, with a report[9] that confirmed it to be of earlier origin having been found in earlier strata than that of Greek black pottery level, it was concluded that this was a separate and unique pottery tradition older than Greek black pottery. The NBPW is deluxe ware associated with mainly table ware. It was related with the aristocratic class and was not in public use[10]. This pottery has a wide distribution in the Indian subcontinent[10,11] (Figure 1).

The identification of the colouring agent of the black coating of NBPW and its characteristic glow has been a subject of inquiry. Sanaullah[12] reported that its black coating has about 13% Fe_2O_3 which is responsible for black shade and that the coating is not the siliceous glaze. He also mentioned that ferrous silicate is responsible for the colour effect. To account for the lustre, he assumed the formation of ferrous lime and ferrous magnesia silicate, which bring about the fusion of the black film during firing, being of low fusibility. Further, he suggested the possibility of the deposition of carbon and terra matter in the pores to enhance the black colour[12]. On the basis of his observations, Lal[13] hypothesized that the black gloss of NBPW was due to some sort of post-firing treatment in which kiln-hot pottery was coated with some organic liquid of vegetable or animal origin, but the exact method of firing and nature of the proposed ferruginous material employed in its manufacture still remain elusive. Hegde[14] suggested that the shining black slip has originated from a thin layer of black magnetic oxide, Fe_3O_4,

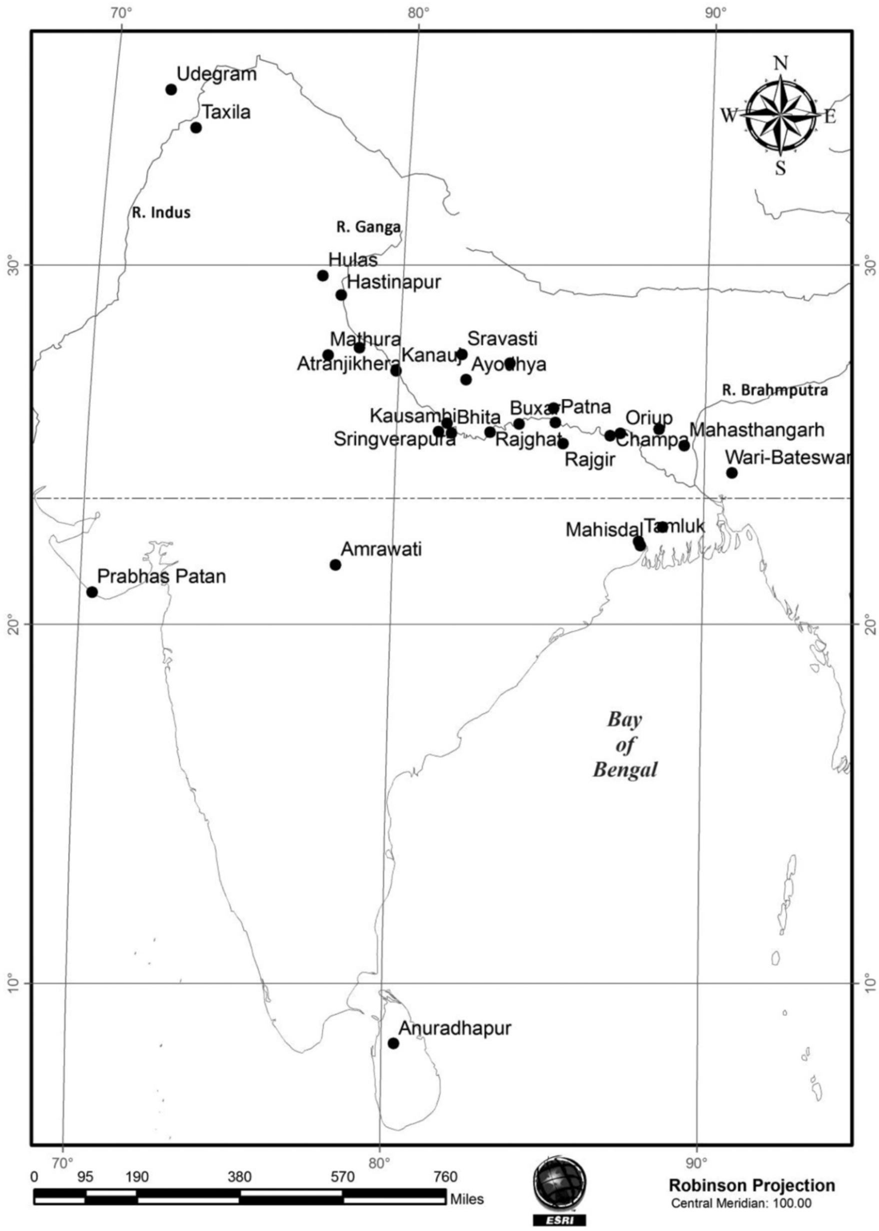

Figure 1. Map showing major archaeological sites of northern black polished ware (NBPW) and horizon of NBPW.

which is also responsible for its black colour. He also suggested the formation of glass-like substance. Due to the tendency of slip to crack, he suggested that the slip was applied on baked clay[14]. In contradiction to the Hegde's view, Bimson suggested that NBPW was mistaken for Greek black gloss and pointed out several differences. Thus, a razor will run smoothly across the Greek black, whereas it will cut into the Indian black (NBPW). While Greek black is magnetic, NBPW is relatively non-magnetic. Greek black gloss stands the 1000°C without any change, while Indian black gloss shows considerable variation in its resistance to such a high temperature. Bimson also suggested that bright gloss is not a glaze or lacquer. The ridged areas showed that the shiny surface is not confined to the raised parts in microscopic examination, but its appearance may be related to some characteristics of the material used for the surface layer as found to be the case with Greek black gloss[15]. The British Museum Laboratory does not agree with the view of burnishing and suggests that the unfired pots were dipped in a suspension of ferruginous inorganic material, probably resembling a red earth and after firing to a temperature of 800°C, the kiln was sealed so that the pots cooled in a reducing atmosphere. According to the investigators, the precise nature of the surface layer still remains unresolved. Bhardwaj[16] tried to separate the slip

Table 1. Weight percentage and atomic percentage of the elements present in the samples

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
Element	Std. wt%	Std. at%	Std. wt%	Std. at%	Std. wt%	Std. at%	Std. wt%	Std. at%	Std. wt%	Std. at%
Ca	1.09	0.55	4.04	3.18	0.67	0.33	0.64	0.33	0.49	0.25
K	3.21	1.67	6.51	5.26	2.39	1.24	2.95	1.57	4.98	2.60
Fe	4.58	1.67	17.47	9.88	4.25	1.54	8.86	3.30	3.88	1.42
Ti	0.77	0.33	1.33	0.88	1.53	0.64	0.47	0.20	0.43	0.18
Al	8.69	6.57	20.94	24.52	7.72	5.77	12.51	9.64	11.85	8.97
Si	25.52	18.52	45.75	51.45	25.71	18.46	19.39	14.35	22.88	16.64
Mg	1.31	1.10	2.15	2.80	1.20	0.99	1.34	1.14	1.50	1.26
Na	0.65	0.57	0.55	0.75	0.29	0.25	0.74	0.67	0.28	0.25
O	54.18	69.02	0.00	0.00	56.08	70.67	52.82	68.62	53.50	68.30
P	0.00	0.00	1.26	1.28	0.16	0.11	0.09	0.06	0.10	0.07
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.10	0.11	0.06
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02	0.00	0.00
Total	100	100	100	100	100	100	100.02	100	100	100

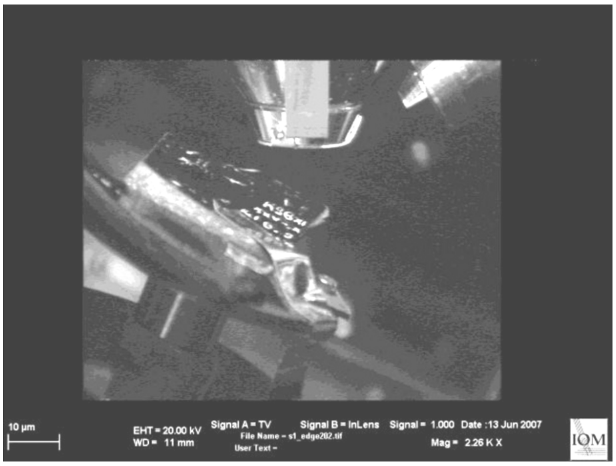

Figure 2. Pottery mounted in SEM chamber for characterization.

from the surface of NBPW. He treated the slip with hydrofluoric acid and observed that a thin layer of the surface had been detached. He analysed the slip and showed that it was due to the application of refined clay (sajjamatti) and organic liquid before burning. This result is in agreement with that of Lal[13], who also suggested that slip was due to post-firing treatment of the pottery.

While the views of Sanaullah may be taken to suggest that ferrous silicate is chiefly responsible for the colour effect, which might have been enhanced by the deposition of carbon and tarry matter[17], the views of Lal may suggest that post-firing application of organic material on the hot pottery is chiefly responsible for the lustrous black[12,13]. In a recent study, application of organic substance to create glaze has also been reported[18]. In a comparative study through binocular microscopic observation and SEM, Sharmin and Okada[18] found two distinct layers on the surface of the pottery, suggesting application of two kinds of slip on NBPW to create glaze. Hegde claims that black colour is due to magnetic oxide of iron (Fe_3O_4) and the lustre is due to a glass-like substance. Bimson's observation contradicts Hegde's assertion, but without providing plausible explanation to substantiate the claim.

Analysis of two sherds from Kausambi and Rajgir was carried out by Gills and Urch[19]. One was dark black glossy on one side with bronze being in the inner side, whereas the samples from Rajgir had bronze metallic slip on both the sides, i.e. inner and outer surfaces. They used X-ray photoelectron spectroscope (XPS) analysis and average SEM probe analysis for study and concluded that the black colouration of NBPW is due to the presence of iron-rich biotite or related mica. They have suggested that the glossy surface was due to the destruction of clay mineral by the sintering of slip and the characteristic gloss was a product of mica platelets aligning themselves parallel to the surface of the slip. The four NBP potsherds were examined by Harding[20] in order to study the probable cause of glazing. He suggested a three-fold process of firing in which oxidation, reduction and reoxidation take place, which is responsible for the creation of glossy slip over the surface of pottery. Nevertheless, none of these studies corroborates a satisfactory reason for firing temperature and resulting glaze of NBP potsherds.

Information about methods of pottery production can be obtained by studying void and inclusion orientation using radiography[21,22], thin-section petrology[23,24] or SEM examination of polished[25–27] or fractured section[25,26,28]. The examination of a polished section of the body and surface of a pot sherd using SEM with attached analytical facility provides a powerful technique for studying many of these surface treatments[27]. Elemental mapping constitutes a significant role in the analysis of spatial distribution and precise identification of elements at the surface of the artefacts[29]. SEM attached with EDS provides rapid and excellent elemental map with routine sample preparation[30].

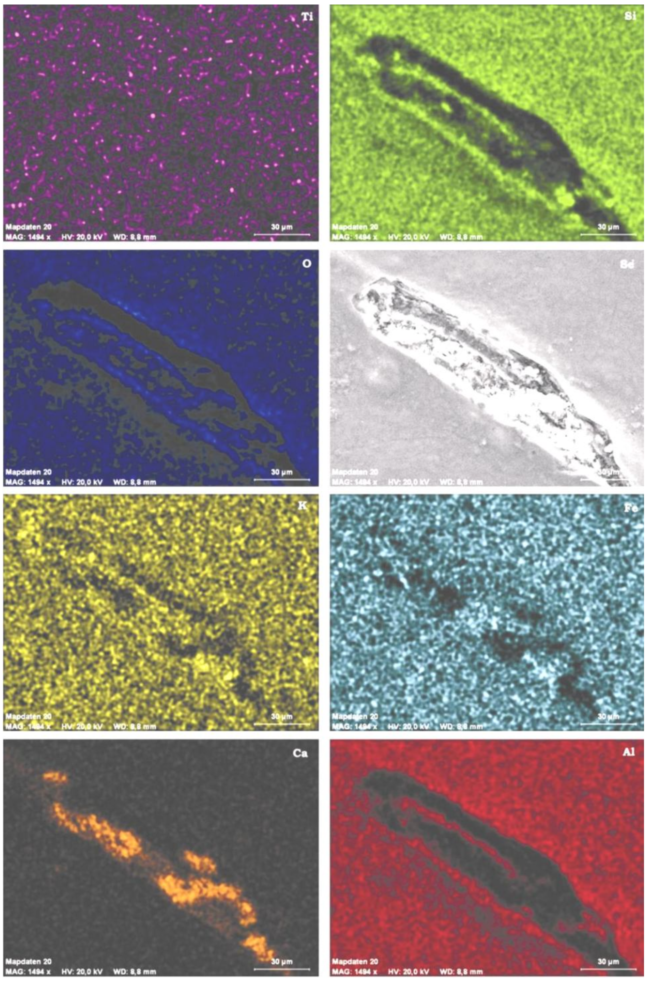

Figure 3. Elements present at the surface of the pottery.

Modern instrumental methods have significant application in the characterization of archaeological pot sherds[31]. In order to study the outer glossy surface, analysis has been carried out at three locations, namely outer surface, very fine outer layer and core beneath the outer layer. All the samples were black in colour and the surface was shining. All were made of well-levigated clay and produced a metallic sound. The samples were selected in order to ensure that these would represent the available assemblage and so they were selected in a random manner[32]. A total of seven pot sherds from Kausambi were selected in which two were analysed at Leibniz-Institut für Oberflächenmodifizierung, Germany (by Jürgen Werner Gerlach) and the rest five were analysed at Nano-Phospher Application Centre, University of Allahabad. This Nanophosphor Centre is equipped with various cutting-edge instruments, including FEI-made Quanta 200 scanning electron microscope attached with EDAX Genesis energy-dispersive X-ray microanalysis system for elemental analysis, which has been used in this study. FEI Quanta 200 is a high-performance electron microscope which is capable of working in low to very high vacuum imaging mode. It provides simultaneous secondary electron and backscattered electron imaging in low vacuum mode, which is ideal for the analysis of archaeo-materials.

Five among the seven pot sherds recovered from an early historic site, Kausambi[33–35] were examined for high-resolution surface analysis and X-ray microanalysis of elements present in pottery (Table 1). Samples were soaked in distilled water for 12 h and then cleaned smoothly with a brush and dried at 75°C for 24 h. Samples were ground and polished vertically to 1 μm grain size; a fresh scratch was made on the surface of NBPW and then analysed with EDS in order to obtain information about elements present on the surface (Figure 2). Elements were also mapped with elemental mapping facility available with SEM–EDS (Figure 3). The high-resolution images at the scale of 2.55 kx and 2.29 kx were obtained to get information about the minerals present in the core of the pottery. High-resolution SEM images at ascending magnification were taken in order to understand microstructure of the surface slip and core, on the one hand and relationship of outer layer with inner core on the other. One sample was ground along with the edge and mapped at different magnifications (Figure 4). Another sample was ground vertically for the study of thickness and fusion of slip with inner core of the pottery (Figure 5) while yet another sample was ground also vertically to study the minerals present in the core of the pottery (Figure 6).

The art of ancient pottery construction within a society led to a slow trial and error process without much of scientific basis. The knowledge thus generated would have often lasted for at least decades, if not longer[36]. Choosing raw material was another important aspect in pottery. The availability of raw material has been a major concern for potters[11,37] and the supply of raw material is often suggested as a method of control of production[3].

Chemically, all clays are composed of oxides of silicon, aluminum and hydrogen, namely, silicon dioxide, aluminum trioxide and water in a weight proportion[38]. During the study of the outer surface a fresh scratch was made and analysed with EDS and elemental mapping was performed at the magnification of ≈1.5 kx and 20 kv voltage. Ti is found equally distributed at the surface, whereas K and Fe showed slight variation in the outer slip and scratch. The most wide variation was seen in the case of Se, Si, O, Al and Ca. Variation in the concentration of Se, Si, O, Al and Ca between the surface and the scratch was large; so this could provide a clue for slip analysis (Figure 3).

Se is a non-metal element of the sulphur group and is frequently found in soils[39]. Si and Al are the main constituents of clay. Si is semi-metallic and Al is a metallic element. Both are present in the outer surface and in the core of pottery, but not in the core of the outer layer.

Both K and Fe are present homogeneously on the outer surface, outer thin layer and in the core. X-ray micro-

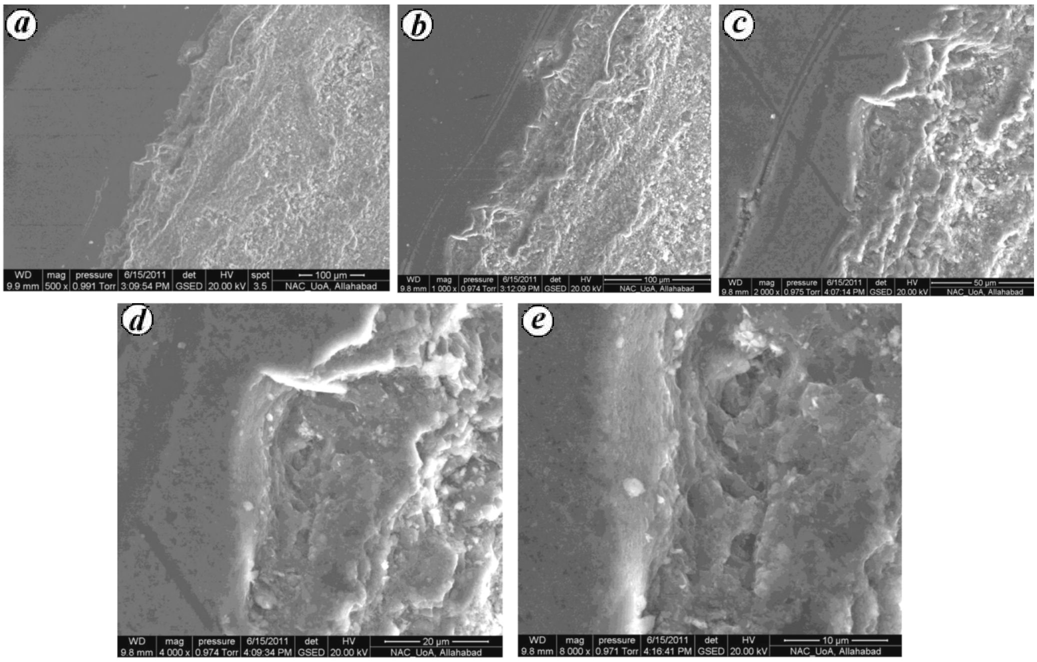

Figure 4. SEM photomicrographs of pottery ridge at different magnifications. ***a***, 500×; ***b***, 1000×; ***c***, 2000×; ***d***, 4000×; ***e***, 8000×.

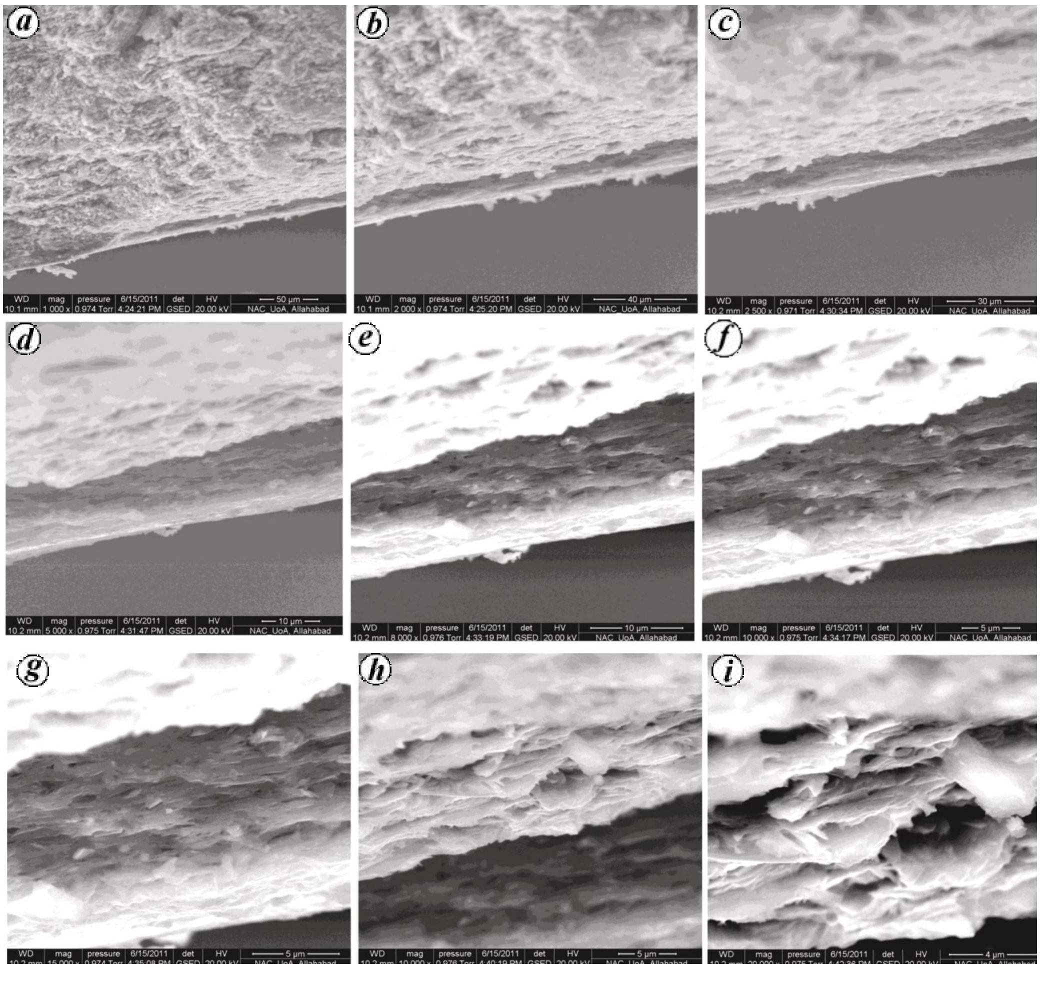

Figure 5. SEM photomicrographs of outer black layer of pottery at different magnifications. ***a***, 1000×; ***b***, 2000×; ***c***, 2500×; ***d***, 5000×; ***e***, 8000×; ***f***, 10,000×; ***g***, clay minerals of black layer at 15,000× magnification; ***h***, clay minerals beneath the black layer at 10,000× magnification; ***i***, clay minerals beneath the black layer at 20,000× magnification.

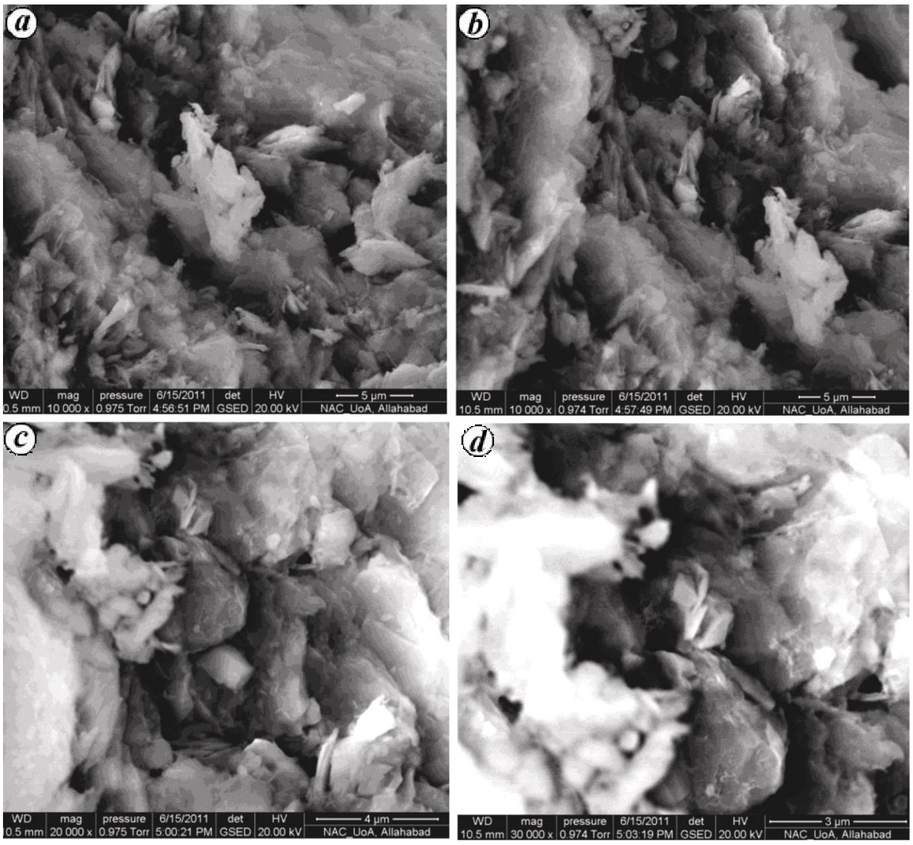

Figure 6. SEM photomicrographs of core of pottery at different magnifications. ***a***, 10,000×; ***b***, 10,000×; ***c***, 20,000×; ***d***, 30,000×.

analysis of core and edge showed that in all cases the K peak was higher than the Fe peak. Si and Al along with K and Fe were associated with clay-forming minerals. Ca was neither present at the outer surface nor in the outer slip, but was in good quantity in the core of pottery. Perhaps it had decomposed from the surface during firing process. The samples were highly oxidized, so traces of oxygen were visible in the entire pottery.

SEM images in ascending order of magnification showed that the outer surface of the slip was amazingly smooth, but there was no evidence of any kind of slip. The outer glossy surface was entirely fused with the core of pottery (Figure 5 *c* and *d*). This indicates that some kind of solution had been used before firing of the pottery and during firing process it fused with the surface of pottery. That is why no traces of slip were available in SEM images. Most probably, these pots have been prepared on fast-rotating wheels and some leather-like material may have been used for giving the finishing touch at the outer surface. Traces of mica platelets, aligning themselves parallel to the surface of the slip was not found, which has been suggested as a reason for the glossy surface by Gills and Urch.

The study of SEM photomicrographs showed that no post-firing slip was applied on the surface of the pottery. In order to produce gloss on the surface, some kind of pre-firing treatment had been carried out with fine particle solution which was decomposed and completely fused with the core of the pottery. It is 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, but distinctive glossy finish of NBPW still needs revision. The ancient potters used locally available clay to manufacture this special kind of pottery and the technology of production was a sophisticated one. The knowledge of manufacturing technology was restricted to a special groups of potters, but disappeared with the passage of time.

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IGMIS – a computer-aided information system on Indian Gondwana megaspores

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The Indian Gondwana Megaspore Information System (IGMIS) is an information system developed for storage and retrieval of Indian Gondwana megaspore (female reproductive unit of early land plants) records in a selective manner. At present, it provides information on 45 genera and 159 species recorded from Palaeozoic and Mesozoic sediments of India. The use of the database is to store and organize information on Indian Gondwana megaspores accrued over the past 70 years. This information system is a significant step towards ensuring safety and accessibility of the data on the dispersed Indian fossil megaspores, besides providing accessibility for handling the information in

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