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Original article

A study of archaeological pottery of Northeast India using laser induced breakdown spectroscopy (LIBS)

Pankaj Singh [a,*], Eshita Mal [b], Alika Khare [b], Sukanya Sharma [a]

[a] Department of Humanities and Social Sciences, Indian Institute of Technology Guwahati, India
[b] Department of Physics, Indian Institute of Technology Guwahati, India

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ABSTRACT

The objective of this work is to investigate the chemical composition of the archaeological potsherds from Northeast India. Laser breakdown spectroscopy (LIBS) and scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDX) have been used to identify the chemical composition of potsherds. LIBS is a micro-destructive technique and based on the time resolved detection of optical emission of transient plasma. In archaeological science, application of LIBS has gained interest for its capability in atomic species recognition. Scanning electron microscope coupled with energy dispersive X-ray spectroscopy are powerful techniques to investigate the microstructure as well as the chemical composition of the archaeological ceramics. LIBS and EDX analyses have revealed that divergent quantities of Si, Al, Fe, Mg, Ti and K occurred as key constituent in the composition of analysed potsherds. The SEM-EDX results demonstrate that low refractory and non-calcareous clay have been used as raw material and the pottery was fired below 800 °C.

1. Introduction

The study of provenance, manufacturing techniques and raw materials of ancient artefacts may provide valuable and meaningful information to the archaeologists. For example, the chemical and mineralogical analysis of pottery from a particular location can give information regarding the origin or source that allows scholars to enlighten about the communication, trade and partnership with other locations. Thus, it provides information regarding the available techniques in processing materials and subsequently in obtaining the final product [1]. According to Giakoumaki et al. [2], investigating and determining the chemical properties of artefacts is one of the most common aims for the archaeologists.

In recent decades, there has been growing application of scientific methods in the field of archaeology. The interdisciplinary approach of archaeology has been significantly encouraged by the archaeologists and is now considered as an integral part of archaeological studies. For example, Fourier transform infrared (FTIR), X-ray diffraction (XRD), thin section petrography, Raman spectroscopy, scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX), X-ray fluorescence (XRF), proton-induced X-ray emission (PIXE), induced coupled plasma mass spectroscopy (ICP-MS), and laser induced breakdown spectroscopy (LIBS), etc. are the most used techniques in archaeological science [1–3].

The laser induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy (LIPS) is an optical emission spectroscopic technique [4]. During last few years LIBS has registered great potential towards rapid qualitative as well as quantitative analysis of samples [1,4]. When high intensity, pulsed laser of short duration is focused on to a material, it produces plasma commonly termed as laser-induced plasma (LIP). By measuring the spectral emission from the laser induced plasma, qualitative as well as quantitative information about the material can be obtained. This spectroscopic analytic technique is known as laser induced breakdown spectroscopy (LIBS) [2,4,5].

In recent years, LIBS has received an increasing attention due to some special features making it a unique technique [2]. These special features are free from any kind of sample preparation, applicable to any sample irrespective of its physical states, nearly non-destructive, applicable for multi-elemental analysis, applicable over wide spectral range (UV, visible, and NIR regions), simple, inexpensive compact and portable [2,5,6]. It requires only optical access to the sample and hence is also capable of online analysis of hazardous material. LIBS has many fold applications in almost every branch of science like restoration and conservation of cultural heritage, determination of the contamination of environmental i.e. hazardous and toxic element from industrial plants, study of soil,

* Corresponding author.
E-mail address: mpankaj.singh26@gmail.com (P. Singh).

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detection of trace element in food specially in vegetable which is in direct contact with polluted soil water and air, forensic applications, etc. [2,4].

Giakoumaki et al. [2] give an extensive review on basic principle and techniques of LIBS and its applicability in analysis of cultural heritage including painted artworks, icons, polychromes, pottery, sculpture, and metal, glass, and stone artefacts. Anglos [5] studied the element of pigments of various cultural heritage object using LIBS. Ponterio et al. [6] use LIBS technique to find out the elemental composition of pigment used in decorative purpose of Roman Domus. Gaudiuso et al. [7] have studied the composition of brooches, from the era of VI century BC to VI-VII century AD of Egnatia. In archaeological science, application of LIBS has gained interest for its capability in atomic species recognition [4,8–11]. The mobility, rapid spectra recording and speedy data interpretation make LIBS a unique analytical technique which is useful for the investigation of immovable heritage objects such as museums, conservation laboratories and in situ at historical and archaeological sites [12–14]. According to Khedr and Harith [3], LIBS is having an advantage in terms of high sensitivity, selectiveness, transportability and short measurement time and also provides microscopic resolution, depth profiling and multi-elemental investigation.

The Neolithic period of Northeast India is known for the cord-marked pottery associated with the shouldered Celts. The earliest date of the Neolithic period of Northeast India comes from the site of Ranyak Khen, Nagaland dated 5560 ± 40 BP (Beta-260242) [15] and the latest date is from Gawak Abri, Garo Hills, Meghalaya which is 2.3 ± 0.2 (LD 1727) [16]. The archaeological site of Ambari is dated to 1030 ± 130 AD [17,18] and Sri Sri Suryapahar is stylistically dated between 10th and 12th Century AD.

Chemical composition of five Neolithic and five Historical potsherds (Fig. 1) have been examined using laser induced breakdown spectroscopy (LIBS) and energy dispersive X-ray (EDX) techniques. EDX analysis provides the percentage of key elements in the ceramic properties. Selected Neolithic potsherds are from Barapani (BRP) and Sawmer (SMR)-Meghalaya; Nongpok Keithelmanbi (KM) and Napachik (NPC)-Manipur; Ranyek Khen (RYK)-Nagaland. In addition, Historical potsherds are chosen from Ambari (AMB) and Sri Sri Suryapahar (SPR) – Assam and Kangla Fort (KGF) Manipur.

2. Archaeological setting

2.1. Nongpok Keithelmanbi (KM) – Manipur

Location: This site is located on the left bank of the Thoubal River in Manipur.

Description: This site was discovered by O.K. Singh, assisted by S.R. Singh of the Department of Archaeology, Government of Manipur. The archaeological remains discovered from the three different locations at the site are divisible into Palaeolithic, Hoabinhian, and Corded ware and curved paddle impressed ware culture [19].

Pottery: Mostly corded ware pottery is found on the site. Pottery are handmade, ill-fired and heavily weathered. While in many cases the corded surface is also eroded. The cord-mark is found in the form of linear and criss-cross patterns. The pottery is made of fine clay and tempered with sand and a few quartz particles. Most of the potsherds are of red and brown colour [20].

2.2. Napachik (NPC) – Manipur

Location: This site is located on the right bank of Manipur River in Manipur.

Description: This site was discovered by Yumjao Singh in 1981. Typo-technologically, the cultural materials from Napachick can be divided into two phases: (i) edge-ground knife of the Hoabinhian character, and (ii) the fully ground celts, hand-made cord-marked pottery and tripod wares of the Neolithic period [19].

Pottery: The tripod wares characterize the ceramic industry of the Napachik. Total 784 pieces of plain ware, 893 pieces of cord-marked ware, 4 pieces of ring footed ware, 64 pieces of tripod leg ware, etc. were found at the site. The pottery is handmade, fragmentary and fired under low temperature. Decoration is done by beating with cord-wrapped paddle [20].

2.3. Barapani (BRP) – Meghalaya

Barapani is situated about 15 km north of Shillong in Meghalaya. Polished stone axes, flakes, blade tools made of phyllite and pottery are collected from the surface.

2.4. Sawmer (SMR) – Meghalaya

Sawmer is situated in East Khasi Hills district, Meghalaya. The potsherds are cord impressed, plain and curve paddle ware. The major patterns are large/medium/small grooves. These potsherds are mainly collected from the surface.

2.5. Ranyak Khen (RYK) – Nagaland

Location: Ranyak Khen (RYK) is situated at about 780 m a.s.l. The cave lies 80 m above a small perennial river at Mimi in Nagaland. This is a Neolithic site.

Description: Ranyak Khen is also known as cave no. 2 among the other limestone caves at Mimi. The mouth of the cave facing west is 8.2–9.0 m high and 7.0 m wide, and is well lit. The assemblage found during excavation includes Edge grinding tools of serpentine and limestone made from river pebbles, a few hammer stones, disc-shaped scraper tools, bone tools and cord-marked pottery besides a human burial [19].

2.6. Ambari (AMB) – Assam

Ambari is located in the heart of Guwhati city, Assam. This site was exposed during construction of building of Reserve Bank of India in 1967 [18,21]. Later, Ambari was excavated in different sessions. The potsherds used in the present work are from the excavation of 2008–09 session [21]. In addition, Ambari potsherds belong to period 1 phase-I dated 7th to 11th century AD. This is based on the architectural, structural and sculptural evidences reported from various strata and their similarities/correlation with different sites of India. Both wheel made and handmade pottery were reported during the excavation. Major pottery types are bowls, jars, vase, handi with carination, lota, inkpot, dish, lamp, few smoking pipes etc. Engraved designs are ribbed, basket, criss-cross, crosses, squarer and these design might be made by beating techniques [22].

2.7. Sri Sri Suryapahar (SPR) – Assam

Sri Sri Suryapahar is situated in Goalpara district Assam. The small scale horizontal excavation was carried by D. Bhengra and aided by T.J. Baidya, S.K. Choudhary, P.M. Das, B. Sinha and T.K. Srivastava Archaeological Survey of India, Guwahati Circle. On the basis of excavation four phases of brick structures have reported and this belong to two periods: 6th–7th century and 8th–9th century AD respectively. Pottery have been found from both the period. Major pottery types are basin, smoking pipe, jar, curved bowls, button-knobbed lid, knobbed-lids, spinkler, small lamps and

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