SEM-EDS, PIXE and Raman spectroscopies analysis of Khlong Thom ancient glass bead, southern Thailand

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Abstract. Various colors of glass beads excavated at the Khlong Thom archaeological site in southern Thailand were characterized non-destructively using proton-induced X-ray emission spectroscopy (PIXE), scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDS), and Raman spectroscopy in order to determine the glass composition and production technology in ancient time. The results show that most of them are alkali-based glass matrices. Some of them are high lead-bearing glass. The glass compositions are approximately the same as the Mediterranean, Islamic, and Indian glasses, but with a higher concentration of aluminum. The colors are influenced by transition metal-ion content such as copper, iron, and manganese. High content of lead has been found in the samples with opaque colors, especially the yellow opaque. The corroded and flaked surface of the glass bead has been revealed by SEM. In a comparison of glass composition, it can be proposed that there is some relationship in production technology between Khlong Thom archaeological site and other sites: South-East Asia; South Asia; East Asia; Asia Minor; and South Africa. This information indicates the historical link of both land and maritime networks for long-distance trade and exchange in ancient time.

1. Introduction
Glasses have been used as ornaments and decorations in Thailand for several hundred years, especially glass beads collected from various regions throughout the country. Smaller objects such as glass beads have an influence on the human way of life and importance of archaeology due to their long history. Most of glass beads found in the South and South-East Asia came from India during the end of the 2nd millennium to the beginning of the 1st millennium B.C. [1-4]. Glass beads rapidly became popular as items of adornment and ceremonialism due to their beauty, affordability, transportability, and durability. Different kinds of them were made and exchanged. Many ancient glass beads were found in prehistoric sites in southern, central, and eastern Thailand. Initial findings showed that glass beads had large numbers of shade of colors. Most of them were small annular or globular monochromatic that commonly called Indo-Pacific bead [5].
Khlong Thom (locally well known as Khun Lukpud) is an archaeological site (where was an ancient town during the late pre-historic to early historic periods) located on the western coast of the Thai–Malay Peninsula, Khlong Thom district, Krabi Province, Southern Thailand. The beads, inscribed with Pallava script, were dated to between the 11th–14th centuries B.C. This is the period of Dvaravati when Khlong Thom was thriving as a trading port for seafarers who traded from India to China. They avoided Straits of Melaka during the monsoon season by making their way across Isthmus of Kra from Khlong Thom to the old town of Nakhon Si Thammarat and advance towards China. From archaeological resources, it is suggested that Khlong Thom is the earliest site for glass production in the 4th century AD [6, 7].

A technique used for analysis should be very sensitive, spatially resolved, multi-elemental, and versatile due to the complex structure of material and it was the object of cultural heritage. Moreover, the technique should be nondestructive and capable of giving complementary information at different scales ranging from macro- to nanoscales. Quantitative analyses of major, minor, and trace elements of archaeological materials are required for deep understanding of manufacturing technology, raw materials, origin of these objects, and their restoration and protective conservation [8–10]. Many X-ray based techniques have been used for analysis of the glass composition include: X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), proton induced X-Ray emission (PIXE), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) [8, 11-13]. In addition, it is well known that Raman spectroscopy is a powerful tool for analysis of the archaeological glasses both for surface weathering study and bulk structure characterization [14-15]. This study reports on composition and production technology of ancient Thai glass bead from the Khlong Thom Archaeological site. The relationship between the Khlong Thom archaeological site and other sites: South-East Asia; South Asia; East Asia; Asia Minor; and South Africa are revealed.

2. Experimental

2.1 Sample

![Figure 1](image1.png)

**Figure 1.** Glass bead samples from the Khlong Thom archaeological site, Krabi Province, southern Thailand

Thirteen ancient glass bead samples with different colors such as blue, green, yellow, violet, and reddish brown which were found in Khlong Thom were labelled as BLP as shown in Figure 1(a). Their chemical composition was characterized using PIXE and SEM-EDS. Six samples with different colors were also
selected for composition analysis by using Raman spectroscopy (Figure 1(b)). Most of the bead samples had annular shape, monochrome color, and a lot of bubbles on surface as illustrated in Table 1. The sample diameter and thickness are in the range of 2-4 mm. Only non-destructive preparation was allowed for these samples due to their archaeological importance. Samples were only cleaned with distilled water and then dried in air at 50°C for 24 h.

2.2 Methods

2.2.1 Chemical composition

2.2.1.1 SEM-EDS. A Hitachi SU-1500 SEM combined with a Horiba Emax EDXRF analytical system (at the COAX Group Corporation Ltd., Thailand) with an accelerating voltage of 15 kV, a takeoff angle of 35.0°, an elapsed live time of 50 s, and a magnification of 200X was carried out for chemical composition analysis. The chemical composition was conventionally determined in oxide wt%. For each sample, three X-ray spectra were collected from the surface at different positions.

2.2.1.2 PIXE. PIXE was performed based on a 2 MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator (at the Plasma and Beam Physics Research Facility, Chiang Mai University, Thailand) with 1–mm–diameter collimated proton beam, 10 nA beam current, and Si(Li) type detector. Quantitative analysis of PIXE spectra of the chemical composition \((Z \geq 13)\) were performed and represented as oxide content using GUPIXWIN code [16-21]. The quantitative calibration included the normalization at 100%-x of the sum of oxide, while the value of x is a sum of Na2O and MgO determined by EDS.

2.2.1.3 Comparison between EDS and PIXE. The chemical composition measured using PIXE and EDS were compared prior to analysis of the samples. Optical glasses with known chemical compositions were used as standard references. It was found that the difference of compositions measured using PIXE and EDS were less than 10%. Therefore, PIXE results were able to be compared to EDS [18]. SEM-EDS possesses lower sensitivity for heavy elements. Therefore, PIXE was only used for determination of concentrations of sodium, aluminium, magnesium, and silicon. Silicon with known concentration was treated as an internal standard reference prior to PIXE analysis as conducted in previous research [19-26].

2.2.2 Raman spectroscopy. The Raman spectra of six glass samples were collected in between 200 – 2000 cm⁻¹ in order to investigate basic database of such glasses by using a UV-Raman spectrometer at the Gem and Jewelry Institute of Thailand (Public Organization). The Renishaw InVia Micro-Raman Spectrometer was operated with Argon laser beam at 514 nm, 2400 lines/mm, 10 exposure times, 1 accumulation, and 1% power (cross-polar) excitation.

3. Results and discussions

The shape of collected glass beads were similar to those sometime called “indo-pacific beads” which were found in the ancient ports on maritime trade route on the western coast of southern Thailand: PKT (Phu Khao Thong, Ranong) (dated to the 2nd century A.D.); NY (Nang Yon, Phang Nga) (dated to the 2nd century A.D.); and TT (Thung Thuk, Phang Nga) (dated to the 8th century A.D.) sites [27]. PIXE was capable of multi-elemental analysis that having a minimum detectable concentration of approximately 0.1 – 1 ppm. By applying EDS, it was possible to determine the elements that were not detectable by PIXE such as sodium and magnesium. Composition of Khlong Thom glass beads was determined by using a combination of PIXE and EDS, as shown in Table 1: Silica (SiO₂) (60.89 to 79.16 wt%); soda (Na₂O) (0.46 to 14.02 wt%); lime (CaO) (0.38 to 4.94 wt%); potash (K₂O) (2.82 to 21.56 wt%); and magnesia (Mg₂O) (0.14 to 0.38 wt%). As implied by the range of potash and magnesia contents, they were therefore classified as a low-magnesia high-potash (LMHK) glass (even though the contents of potash (> 2 wt%) and magnesia (< 1 wt%) of some samples were slightly out of LMHK range) [28]. The high ratio of K₂O/Na₂O (> 1) showed that most of them were potash glass except BL6P which was mixed alkali glass [29-35]. Other major and minor compositions were also determined: alumina (Al₂O₃) (2.51 to 6.50 wt%); hematite (Fe₂O₃) (0.44 to 2.07 wt%); and manganese oxide (MnO)
(up to 2.96 wt%). The high ratio of MnO/Fe₂O₃ which showed in BLP9 indicated that MnO was intentionally added as a decolorant [36]. Titania (TiO₂), commonly presented as an impurity in sands or silica raw materials [36-37], was found in all samples with a content up to 0.31 wt%. Copper oxide (CuO) (up to 2.25 wt%) and cobalt oxide (CoO) (up to 0.09 wt%) were also found. Litharge (PbO) (up to 18.19 wt%) was detected in the opaque samples, i.e. BLP11, BLP12, and BLP13. It is suggested that high lead concentration found in these samples caused by the using lead as a flux [27, 39-40]. It is well-known that lead–containing glass has been used for decoration for several hundred years [26, 40].

Table 1 Chemical compositions of ancient glass bead samples from the Khlong Thom analyzed using PIXE and SEM-EDS

| Sample | BLP 1 | BLP 2 | BLP 3 | BLP 4 | BLP 5 | BLP 6 | BLP 7 | BLP 8 | BLP 9 | BLP 10 | BLP 11 | BLP 12 | BLP1 3 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Color/shape | greenish blue/round | blue/fragment | greenish blue/round | light blue/round | blue/fragment | blue/round | blue/round | blue/round | violet/round | light blue/round | yellow/tabular | green/tabular | reddish brown/round |
| Na₂O | 0.97 | 1.15 | 0.92 | 0.94 | 0.46 | 14.02 | 2.22 | 4.33 | 1.22 | 1.94 | 1.80 | 0.81 | 2.42 |
| MgO | 0.18 | 0.37 | 0.17 | 0.14 | 0.16 | 0.23 | 0.38 | 0.29 | 0.17 | 0.24 | 0.17 | 0.27 | 0.18 |
| Al₂O₃ | 4.94 | 3.99 | 4.69 | 3.67 | 3.18 | 6.50 | 4.74 | 5.64 | 3.74 | 5.17 | 5.13 | 2.51 | 5.90 |
| SiO₂ | 73.91 | 75.60 | 76.50 | 76.61 | 79.16 | 64.75 | 74.02 | 71.61 | 73.27 | 81.44 | 60.89 | 67.80 | 63.81 |
| S | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| Cl | 0.35 | 0.14 | 0.08 | 0.14 | 0.25 | 0.68 | 0.16 | 0.16 | 0.14 | 0.81 | 0.63 | 0.29 | 0.44 |
| K₂O | 16.75 | 17.42 | 15.95 | 16.79 | 10.10 | 2.82 | 15.17 | 14.95 | 17.86 | 4.71 | 10.03 | 15.58 | 21.56 |
| CaO | 0.45 | 0.60 | 0.55 | 0.38 | 2.05 | 4.94 | 0.76 | 0.62 | 0.61 | 2.28 | 0.84 | 0.77 | 1.76 |
| TiO₂ | 0.20 | 0.16 | 0.17 | 0.14 | 0.24 | 0.31 | 0.12 | 0.20 | 0.16 | 0.26 | 0.25 | 0.11 | 0.30 |
| MnO | 0.03 | 0.08 | 0.04 | 0.61 | 2.28 | 2.96 | 1.46 | 1.02 | 2.13 | 1.15 | N/A | 0.06 | 0.16 |
| Fe₂O₃ | 0.58 | 0.44 | 0.44 | 0.52 | 1.90 | 2.07 | 0.86 | 0.93 | 0.64 | 1.11 | 0.71 | 0.97 | 1.18 |
| CoO | N/A | N/A | N/A | 0.04 | 0.08 | 0.08 | 0.09 | 0.03 | N/A | 0.05 | N/A | N/A | N/A |
| CuO | 1.64 | 0.05 | 0.50 | N/A | 0.13 | 0.04 | 0.04 | 0.12 | 0.04 | 0.04 | N/A | 0.81 | 2.25 |
| ZnO | N/A | 0.01 | N/A | 0.03 | 0.13 | N/A | 0.01 | 0.01 | 0.01 | 0.40 | N/A | N/A | N/A |
| Ar | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| SrO | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| BaO | N/A | N/A | N/A | N/A | N/A | 0.32 | N/A | 0.10 | N/A | N/A | N/A | N/A | N/A |
| PbO | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | 18.19 | 9.80 | 0.82 |
| Total alkali (wt%) | 17.72 | 18.57 | 16.87 | 17.73 | 10.56 | 16.84 | 17.39 | 19.28 | 19.08 | 6.65 | 11.83 | 16.39 | 23.98 |
| K₂O/Na₂O ratio | 17.27 | 15.15 | 17.34 | 17.86 | 21.96 | 0.20 | 6.83 | 3.45 | 14.64 | 2.43 | 5.57 | 19.24 | 8.91 |
| MnO/Fe₂O₃ ratio | 0.06 | 0.19 | 0.09 | 1.18 | 1.20 | 1.43 | 1.70 | 1.10 | 3.33 | 1.04 | 0.00 | 0.07 | 0.14 |

Note: N/A denotes non-detectable (for composition of < 0.01 wt%)
Types of glasses can be identified through the relative intensities of the bands due to \(\text{Si–O}\) stretching (~1000 cm\(^{-1}\)) and \(\text{Si–O–Si}\) bending (~500 cm\(^{-1}\)) modes [42-53]. The high intensity of the bending modes reflected strong connectivity of tetrahedral structures. In weak connectivity of tetrahedral units (caused by the addition of fluxing agents), the intensity of bending mode was diminished and the stretching modes became more intense. Peak shift was found in the spectra of BLP11 and BLP12. It was the characteristic of structure with isolated and poorly connected tetrahedral units. This structure was observed by the glassy network, which contained a large amount of PbO (lead–alkali glass) [47, 54]. In glass production, some transition elements such as copper, iron, cobalt, and gold were added to color production. The red color was also obtained with their high concentration. A combination of copper and cobalt was used for blue coloration. The yellow color was resulted from high contents of iron and lead. Manganese was used for purple coloration [55-56]. Even though the glass beads were colorful, no observation of colorant signal was found in Raman spectra [42, 57]. Only the glassy matrix fingerprint is presented in the Raman spectra. The band in between 1400 – 1600 cm\(^{-1}\) was unclear [53]. Other previous works showed that the band in this range was assigned to deformation vibration of the H–O–H group in structure of glass or surface absorbed water [49]. Furthermore, some of Raman spectra in this work were similar to those of ancient glass beads excavated in South Africa [58].

![Raman spectra](image)

**Figure 2.** Raman spectra of selected ancient glass bead samples from the Khlong Thom archaeological site, Krabi Province, southern Thailand

**Table 2** Raman index of the selected ancient glass bead samples from the Khlong Thom archaeological site, Krabi Province, southern Thailand

| Sample | \(A_{500}/A_{1000}\) |
|--------|------------------|
| BLP3   | 0.45             |
| BLP7   | 0.56             |
| BLP9   | 2.01             |
| BLP11  | 2.18             |
| BLP12  | 0.61             |
| BLP13  | 2.42             |

Raman index (\(A_{500}/A_{1000}\)) is the ratio of the areas under the peaks of 500 and 1000 cm\(^{-1}\), respectively. The index implies information about the network connectivity of modified silica and glass processing temperature: 1400 °C for \(A_{500}/A_{1000} \sim 7\); 1000 °C for \(A_{500}/A_{1000} \sim 1.3\); and 600 °C or below for \(A_{500}/A_{1000} \sim 0.3\) [45, 58-59]. The values of \(A_{500}/A_{1000}\) in Table 2 were shown to be of
between 0.45 to 2.42 which imply the glass processing temperature of between higher than 600 and lower than 1,400 ºC (for \( A_{500}/A_{1000} < 2.4 \)).

4. Conclusion
Ancient glass beads excavated from Khlong Thom, Krabi Province, southern Thailand were successfully investigated by PIXE and SEM-EDS. The combination of these techniques allowed the multi-elemental analysis to be done more accurately. The results demonstrated that their glass productions were at different sites and the use of chemical raw materials. The slightest difference in compositions of glass produced at the same site possibly resulted from variations in the glass production or the use of raw materials from different batches. The elemental analysis results may be affected by weathering and surface leaching contaminations. Such corroded patterns were produced by the interaction of both ground water and its dissolved chemical compounds with the glass surface. In addition, water acidity or basicity also played an important role in the corrosion process of glass. Raman spectroscopy and X-ray fluorescence spectroscopy were used for compositional investigation of some ancient glass beads collected from Khlong Thom archaeological site. It was clear that both alkali–based glass and lead–alkali–based glass were fabricated with similar low temperature–firing process.

Most of the glass beads collected from the Khlong Thom archaeological site contained high alumina and low magnesia which was the characteristic composition of glass produced from South India, South China, and mainland Southeast Asia. Furthermore, the contents of copper, iron, and lead in the opaque red glass was similar to the Roman glass made in the 1st century A.D. These results indicated some relationship in production technology, and trade and exchange networks in ancient time. The study of ancient glass, as a branch of archaeology, has centered on establishing the information and area of production of glass artifacts. Topological classifications, technological observations, and comparative studies serve to clarify the development and cultural interrelationships of various classes of glass objects. Further analysis will be done to elucidate the role of maritime exchange and trade networks.

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