การวิเคราะห์แก้วโบราณในประเทศไทยโดยใช้วิธีการทางนิวเคลียร์

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บทคัดย่อ

เนื่องจากความหลากหลายในตัวโบราณวัตถุ ทำให้การวิเคราะห์จำเป็นที่จะต้องมีความละเอียด แน่นอน และสะดวก เพื่อที่จะให้ได้ผลที่คลาดเคลื่อนน้อยที่สุด และให้ข้อมูลได้ตั้งแต่ในระดับเห็นได้ด้วยตาเปล่าจนถึงระดับนาโนเมตร ในการศึกษานี้ใช้เทคนิค SEM-EDS, PIXE และ SRXRF ในการวิเคราะห์องค์ประกอบทางเคมีของลูกปัดแก้วโบราณที่ขุดค้นจากแหล่งโบราณคดีต่าง ๆ ภายในประเทศไทย ซึ่งลูกปัดแก้วเหล่านี้มีหลายสี และมีเฉดที่แตกต่างกัน ผลการวิเคราะห์พบว่าเนื้อแก้วเป็นทั้งแก้วโซดา แก้วโพแทช แก้วแอลคาไลผสม และแก้วตะกั่ว อย่างไรก็ตาม พบว่าการวิเคราะห์ผลเป็นเรื่องที่ยากมากเนื่องจากอายุที่มากและการถูกกัดกร่อน การศึกษาทำให้ทราบถึงความสัมพันธ์ของการค้าทางทะเลในอดีตระหว่างเอเชียตะวันออกเฉียงใต้ เอเชียใต้ เอเชียตะวันออกและเอเชียกลาง สามารถสรุปได้ว่าโดยรวมแล้ววิธีการทางนิวเคลียร์เหล่านี้ มีประโยชน์ในการวิเคราะห์องค์ประกอบของวัสดุประเภทแก้วและช่วยให้สามารถตอบคำถามของนักโบราณคดีได้เป็นอย่างดี

คำสำคัญ : ลูกปัดแก้วโบราณ SEM-EDS PIXE SRXRF

Nuclear Analytical Methods on Archaeological Glass in Thailand

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Abstract

Due to the complex nature of archaeological objects, their analysis needs to use extremely sensitive, spatially resolved and versatile methods that should be as non invasive as possible and give complementary information at different scales; from the macroscopic to the nanometer scales. In this work, SEM-EDS, PIXE and SRXRF were used to analyze the chemical composition of the archaeological glass bead samples that excavated from various historical sites in Thailand. There were number of differences in shade between the glass beads of different colors. The results revealed different in glass types; soda- and potash-, mixed-alkali-, and lead-based glasses. It was noticed that it has been difficult to interpret because of a long period covering and weathering effects. This study may be led to the historical link of the long distance trade and exchange networks in maritime between South-East Asia, South Asia, East Asia and Asia Minor. These analytical measurements in combination are proved useful to investigate the glassy materials and to answer questions posted by archaeologists.

Keywords: ฬncient glass bead, SEM-EDS, PIXE, SRXRF

1. Introduction

Archaeological glasses have been used as ornaments and decorations in Thailand for several hundred years as seen by archaeological evidences such as glass beads collected from different regions throughout the country.

Glass is mostly found as beads in South and South-East Asia where the earliest evidence of glass comes from the northern part of India and dates from the end of the second millennium to the beginning of the first millennium B.C. [1-3]. Due to their beauty, affordability, transportability and durability, glass beads rapidly became popular as items of adornment and ceremonialism. Different kinds of beads were made and exchanged [4]. For many years, glass beads have been charming and attractive enough for both old and new collections in Thailand. It is the starting point for people who are interested in the origin of the glass beads and the progress of all human societies in the world. Many ancient glass beads were found in prehistoric sites in Thailand. Initials findings suggested that there are different shades among glass beads of different colors.

In this work, the glass bead samples excavated from prehistorical sites such as Hor-Ek (Nakhon Pathom), and Laem Pho and Ban Tha Muang (Surat Thani) were focused and characterized on chemical composition using scanning electron microscope cooperated with energy dispersive X-ray fluorescence spectrometer (SEM-EDS), particle induced X-ray emission spectroscopy (PIXE) and synchrotron radiation to induce x-ray fluorescence (SRXRF).

2. Experiments

The collected samples of ancient glass beads are in tabular or round shapes. The sample size ranges from 5 to 8 mm in diameter and from 2 to 10 mm in thickness. Their shapes are similar as those that sometime called the indo-pacific beads which are found in the ancient ports of the maritime trade route on the western coast of southern Thailand such as Khlong Thom (Krabi), Phu Khao Thong (Ranong), and Nang Yon and Thung Thuk (Phang-nga) [5].

No sample preparation on the surface was possible, because of the non-destructive analysis. Chemical compositions of the glass bead samples were characterized using SEM/EDS, a Hitachi SU-1500 SEM combined with a Horiba Emax EDXRF analytical system with an accelerating voltage of 15 kV. For each sample, three X-ray spectra were corrected at three different positions.

Their chemical compositions were also analyzed using PIXE based on a 2-MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator. The proton beam was collimated with a diameter of 1 mm, and the beam current on the sample was 10 nA. The detector used was of Si(Li) type. Quantitative analysis of PIXE spectra of the chemical composition ($Z \geq 13$) in the samples were performed using GUPIXWIN code. The quantitative calibration included the normalization at (100%-x) of the oxide sum, while the value of x is a sum of Na_2O and MgO determined by EDS.

Prior to the analysis of the samples, their chemical compositions measured using PIXE and EDS were compared. The standards used were optical glasses with known chemical compositions. It was found that the relative errors of the measured values for PIXE and EDS were less than 10 %. Results from PIXE, therefore, could be compared to those from EDS.

A preliminary non-destructive characterization of these samples using SRXRF was carried out in order to confirm the presence of elements. Pb- and Cu-foils were used as the references. The X-ray beam was of 1x10 mm rectangular shape. All measurements were carried out in fluorescent mode. The X-ray photon energy was selected using a Ge(220) double crystal monochromator. All spectra were energy-calibrated with respect to the absorption edge of Pb foil at 3851 eV (±0.2 eV) and Cu foil at 8979 eV (±0.2 eV) with time steps of 1 sec. A 13-element Ge detector was used in these measurements.

3. Results and Discussions

Table 1 shows the chemical composition of the glass bead samples in calculated and weight percentage. Results for Hor-Ek glass beads showed silica (SiO_2) content ranged from 41.80 to 64.92 wt%, soda (Na_2O) and lime (CaO) concentrations were between 1.18 to 14.52 wt% and 1.74 to 2.70 wt%, respectively while the concentrations of potash (K_2O) and magnesia (MgO) ranged from 2.67 to 4.40 wt% and 0.18 to 0.78 wt%, respectively. As implied by the range of the potash and magnesia, all contained potash content above 2 wt% and magnesia content above 1 wt%, thus, they could be classed as a low-magnesia, high-potash (LMHK) glass [6].

The chemical analysis of the Laem Pho and Ban Tha Muang glass beads excepted BTM2 showed that many were very similar in terms of SiO_2, Al_2O_3, CaO, MgO and TiO_2 contents, suggesting that they were each made from a similar sands, perhaps from the same area. The type of the bead glass samples from Laem Pho was found to be the potassium-silica based glass, whiles those from Ban Tha Muang was sodium-silica based one. Both contained low magnesia and high alumina.

Titanium oxide, common impurity in sand, was present with similar concentration in the samples.

The glasses were colored by large amount of oxides of iron, copper and cobalt. Iron oxide may be an impurity in sand raw material or added as colorant. The opacity may be due to bubbles or non-fully dissolved compositions such as SiO_2 or TiO_2. PbO was only found in the samples. High ratio of the concentration of manganese oxide and ferric oxide indicated that it was intentionally added as a decolorant [4, 7].

4. Summary

The glass bead analyses presented demonstrate the long distance trade or exchange network of the ancient time running not only overland, but also the maritime.

The results demonstrated that their glass productions were at difference sites and the use of chemically raw materials. At the same site, slight compositional differences between glass samples may be a result of variables in glass production or the use of chemically similar raw materials with different batches. Any results for light elements would have been unreliable because of the non-destructive analysis. Results from composition analysis may have been 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.

It was shown that the combination of various analytical methods is a powerful tool with which to answer the questions posed by archaeology.

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Table 1 Chemical composition analysis of the glass bead samples using PIXE and SEM-EDS

Name	Description	Composition; SEM-EDS and PIXE (wt%)											
		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	PbO
A008	Red opaque	14.52	0.32	10.22	41.80	3.49	2.24	0.26	0.18	1.97	0.01	0.33	20.11
A053	Red opaque	12.07	0.18	9.63	51.72	4.32	2.22	0.83	0.29	1.69	0.09	1.26	7.47
B123	Red opaque	11.35	0.78	9.06	47.85	3.04	1.74	0.62	0.05	2.68	<0.01	3.34	12.23
C029	Red opaque	13.05	0.54	11.14	46.68	3.40	2.50	0.23	0.23	3.58	0.11	2.82	8.82
C064	Red opaque	13.54	0.51	12.40	52.02	4.00	2.01	0.30	0.12	2.86	0.08	1.19	5.56
A022	Light blue transparent	6.56	0.28	9.72	63.47	3.05	2.70	0.51	0.20	1.32	0.10	0.55	6.64
A025	Light blue transparent	11.01	0.28	10.41	58.96	3.97	2.06	0.38	0.01	1.27	0.01	0.63	3.64
B027	Light blue transparent	6.72	0.48	9.61	50.60	3.24	1.93	0.12	0.12	1.20	0.29	0.68	18.96
C051	Dark blue translucent	2.87	0.48	9.95	64.92	3.11	2.76	0.52	0.21	1.35	1.02	0.56	6.79
C055	Dark blue translucent	8.26	0.45	11.49	58.47	4.40	2.26	0.36	0.25	2.03	<0.01	0.40	5.25
D004	Blue-green transparent	8.93	0.65	9.38	57.13	3.60	2.27	0.40	0.19	1.61	0.27	0.94	7.56
D040	Blue-green transparent	1.18	0.23	11.07	62.96	2.67	2.46	0.45	0.39	2.47	0.46	1.06	8.76
BPR2	Dark blue translucent	17.89	0.14	3.06	73.13	1.70	2.12	0.22	0.70	0.61	0.03	0.10	<0.01
BPR3	Dark blue translucent	18.75	0.21	3.55	68.42	1.30	2.12	0.24	1.26	3.58	0.04	0.02	<0.01
BPR4	Dark blue translucent	17.68	0.18	3.60	69.20	1.80	2.06	0.39	0.89	3.59	0.03	0.13	<0.01
BTM2	Dark blue translucent	0.21	0.26	1.43	75.51	17.11	0.97	0.18	1.73	1.89	0.07	0.03	<0.01
BTM3	Dark blue translucent	0.28	0.22	3.46	75.43	16.63	0.91	0.15	0.54	1.71	0.03	0.13	<0.01
BTM6	Dark blue translucent	<0.01	0.18	3.78	74.24	16.89	0.49	0.11	0.17	0.58	0.03	2.98	0.39

Note: Hor-Ek (A, B, C and D), Laem Pho (BPR) and Ban Tha Muang (BTM)