X-ray spectroscopy study on Thai amulet of Phra Kru Nadune

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Abstract. Thai Amulets are found in many forms in Thailand. They have been made by many different ethnic groups with different traditions. Phra Kru Nadune is one of the important amulets created in Dvaravati period that has been found at Nadune district, Mahasarakham province, northeastern Thailand. Many molds which are all terracotta have been used for production. Microstructure and composition of selected samples of the ancient amulets and the imitative one have been characterized using scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS) and proton-induced X-ray emission spectroscopy (PIXE). The results show that many elements are present as major (C, O, and Si), minor (Na, Al, K, Ca, Fe, Cu, and Zn), and trace elements (Mg, P, S, Ti, Cr, and Mn). Quartz, rice husk, orthoclase, anhydrite, and laterite are the base components, while zinc, copper, and bauxite are the characteristic components. These non-destructive techniques show obvious composition difference between the ancient (original) and new (imitative) amulets.

1 Introduction

Most of people in Asia especially Thailand, Malaysia, Singapore, and China are Buddhists who believe in the sanctity of amulets. The sanctity includes a mystical power of providing happiness and fulfilling salvation of dangers. In Thailand, many ancient amulets are highly revered and demanded by people resulting in possession of very high prices and the production of imitations that are very similar to the originals.

Phra Kru Nadune is one of the ancient amulets created in Dvaravati period (7^{th} - 11^{th} century A.D.). It has been found at Nadune district, Mahasarakham province, northeastern

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Thailand. The amulet has been produced in many shapes including rectangle, curved top square, isosceles triangle, leaf triangle, square, and round-relief. Most of them are terracotta possessing different colors of texture including brown, yellow, red, gray, and pink. This possession is due to raw materials of laterite, rice husk, sand, and clay are burnt in an open-air furnace in which the temperature is unstable. Our previous works have been focused on the composition and morphology analyses of other Thai amulets such as Phra Somdej Wat Rakhang [1-2] and Phra Luang Pho Thuad [3]. In this work, the morphology and composition of Phra Kru Nadune amulets have been analyzed using scanning electron microscopy equiped with energy-dispersive X-ray spectroscopy (SEM-EDS) and protoninduced X-ray emission spectroscopy (PIXE) for examination of the imitative amulet.

2 Experimental

2.1 Sample preparation

8 samples of Phra Kru Nadune amulets (PND2, PND3, PND4, PND5, PND6, PND7, PND8, and PND9) with approximately 1-2 cm in base width and 5 cm in height were examined. These round-relief molded figures were produced in different batches with the same shape called "Nakprok Diao" which means "single Buddha image overspread with a great serpent" as shown in Figure 1.

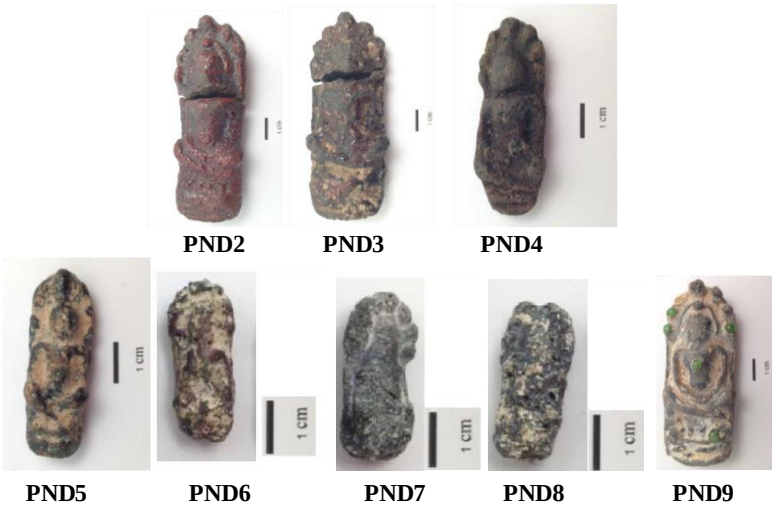

Fig. 1. Samples of Phra Kru Nadune amulets.

2.2 Characterization

2.2.1 SEM-EDS

Morphology and chemical composition were examined using Quanta 450 SEM equiped with X-Max EDS incorporated with INCA software. The operation was done with accelerating voltage of 5 kV. The chemical composition was determined in wt% and

normalized to 100%. Each sample was probed in 3 positions of great serpent, chest, and base. The content of some trace element with approximately 0.01 wt% or lower was not able to be confirmed by SEM-EDS. This element was analyzed only by PIXE.

2.2.2 PIXE

PIXE was operated with 2-MeV-proton beam produced by 1.7 MV tandem Tandetron accelerator. The proton beam was collimated by a diaphragm of 1 mm in diameter in order to generate the beam current of 10 nA on sample. The characteristic X-ray was detected by Si(Li) detector. The sample was probed in the same positions (of great serpent, chest, and base) as examined by SEM-EDS. The chemical composition (for element with $Z \geq 11$) analyzed from PIXE spectra was performed using GUPIXWIN code [4-6]. The normalization of composition was done with 100%-*x* of the total amount of oxides, where the value of *x* was the sum of Na_2O and MgO determined by EDS. The subtraction of *x* was due to low accuracy in detection of Na and Mg by PIXE when compared to other elements with $Z \geq 13$.

The calibration of chemical compositions measured using PIXE and EDS was done before analysis of samples. The optical glasses with known chemical compositions were used as the references. It was found that the relative errors in calibration of the two techniques were less than 10%. The PIXE results can be therefore compared to EDS and the average content of each element from two techniques was evaluated [6]. Silicon with known composition was used as a reference for PIXE analysis as conducted in previous research [1-2,7-18]. The setup of samples for SEM-EDS and PIXE analyses are shown in Figure 2.

(a) **(b)**

Fig. 2. Setup of samples for (a) SEM-EDS and (b) PIXE analyses.

3 Results and Discussion

Morphologies of Phra Kru Nadune amulets are revealed by SEM images as shown in Figure 3, while the elemental compositions analyzed using EDS and PIXE are shown in Table 1. SEM micrographs show the surfaces with porous structures of cavities, cracks, irregular plate-like granules, and fine particles with a narrow range of size distribution. They also exhibit highly corroded surfaces resulted from environmental and chemical effects during their burial period in soil.

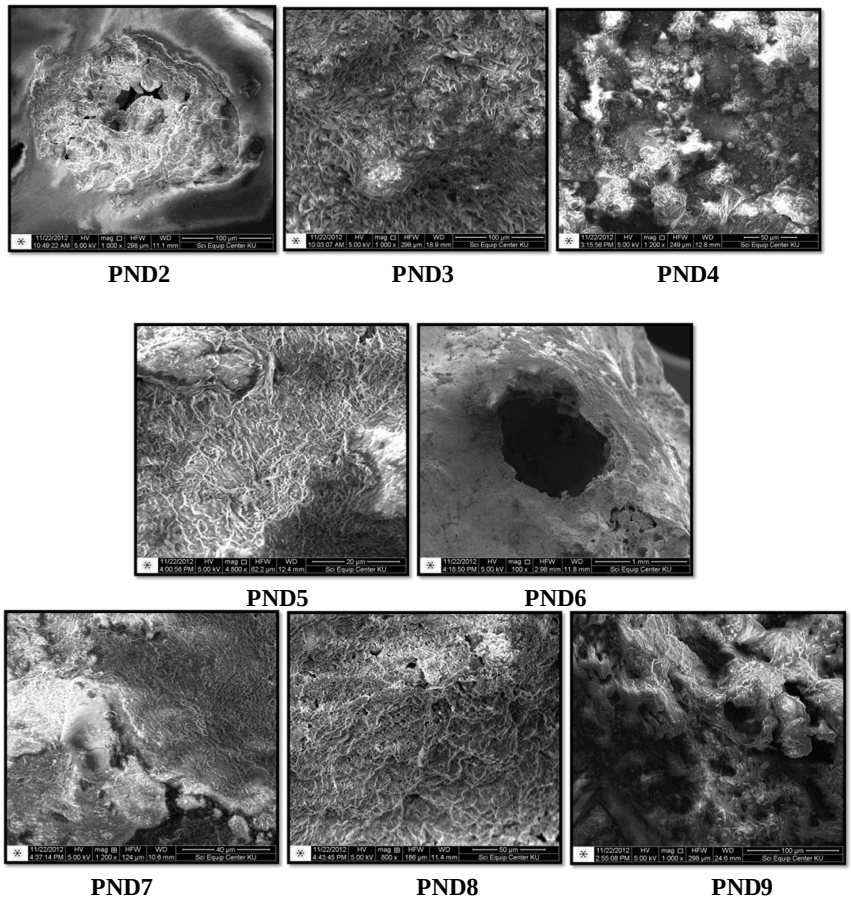

Fig. 3. Morphologies of samples of Phra Kru Nadune amulets.

The composition shown in Table 1 can be used to distinguish the amulets created from different batches of the same mold. The results show that C, O, and Si were the base composition of every samples. Some elements including Na, Mg, Si, K, and Ca were oxidized. SiO_2, Al_2O_3, CaO, S, and Fe were the components of minerals such as quartz, rice husk, orthoclase, anhydrite, laterite, and bauxite. The detection of P was proposed to be come from the burial environment, and minerals and bone ashes which were added to the clay paste [19]. The other oxides and elements (especially C) were present as impurities in raw materials of clay minerals and herb organics. However, B was only found with a high content (approximately 21 wt%) in sample PND3. It is proposed to be in the form of borax (used as a glaze in ceramic production in ancient time), boron silicate mineral (tourmaline), and/or tektite. Furthermore, the composition of sample PND9 was clearly different from the others by possession of larger amounts of Al_2O_3, Mn, and Fe, and smaller amounts of P, S, Cl, Cu, and Zn. The results show that PND9 was the imitative amulet.

It should be noted that the contents of elements such as Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Cu, and Zn are the average of values derived from PIXE and SEM-EDS, trace elements such as Cr and Mn were determined only by PIXE, and the elements such as B, C, and O were only detected by SEM-EDS. The contents of some trace elements in some samples including S (PND9), Cl (PND9), K (PND6 and PND8), Cu (PND9), and Zn (PND9) were analyzed only by PIXE due to the elements were not detected by EDS. This

indicates that the contents were beyond limit of detection of EDS. The high deviations of contents of carbon in every sample and those of SiO_2 and others in some samples reflect the high heterogeneity of materials texture of amulets. The high heterogeneity is proposed to be resulted from ancient indigenous technique of fabrication (~1,000 years ago) in which poor mixing of raw materials was done before shaping of amulet.

4 Conclusion

Non-destructive techniques of SEM-EDS and PIXE were essential for the analysis of Phra Kru Nadune amulets which provided information about the morphology and elemental composition. The results showed high heterogeneity of the amulet textures and composition difference between the ancient (original) and new (imitative) amulets. The results showed that the sample PND9 was the imitative amulet.

Table 1. Composition of Phra Kru Nadune amulets analyzed using SEM-EDS and PIXE.

Element	**Sample/Composition (wt%)**							
	PND2	**PND3**	**PND4**	**PND5**	**PND6**	**PND7**	**PND8**	**PND9**
B: Average	N/A *	21.67	N/A *	N/A *	N/A *	N/A *	N/A *	N/A *
SD		±3.42						
C: Average	27.47	57.55	60.04	42.75	39.41	74.57	62.46	34.57
SD	±5.72	±28.11	±31.66	±23.12	±12.56	±35.12	±25.23	±15.34
Na_2O: Average	1.97	1.78	0.50	0.63	2.68	0.59	3.17	1.11
SD	±0.74	±1.18	±0.19	±0.13	±1.57	±0.31	±1.62	±0.70
MgO: Average	0.77	0.25	0.22	2.71	1.70	0.64	0.42	1.71
SD	±0.36	±0.05	±0.09	±0.81	±1.01	±0.09	±0.29	±1.07
Al_2O_3: Average	0.51	1.78	0.32	5.50	0.79	4.31	1.02	11.77
SD	±0.41	±0.76	±0.19	±2.89	±0.24	±0.07	±0.78	±1.14
SiO2: Average	61.31	6.31	6.73	37.27	48.24	12.02	9.67	42.83
SD	±8.32	±3.40	±1.87	±6.37	±7.31	±4.57	±6.17	±16.85
P: Average	1.12	0.56	0.32	1.73	1.72	0.87	0.59	0.16
SD	±0.28	±0.41	±0.10	±1.10	±0.10	±0.40	±0.26	±0.08
S: Average	0.35	0.49	0.57	1.12	1.38	0.73	0.76	0.0817**
SD	±0.28	±0.29	±0.14	±0.35	±0.43	±0.40	±0.60	±0.0436
Cl: Average	0.44	0.32	0.38	0.26	0.28	0.69	0.13	0.0683**
SD	±0.29	±0.12	±0.19	±0.16	±0.07	±0.37	±0.07	±0.0487
K_2O: Average	0.19	0.24	0.20	0.17	0.0792**	0.25	0.0937	0.31
SD	±0.12	±0.05	±0.08	±0.05	±0.0513	±0.12	±0.0445	±.021
CaO: Average	0.52	2.14	1.12	2.56	1.61	3.39	3.43	1.22
SD	±0.47	±0.93	±1.06	±1.63	±0.91	±1.32	±1.74	±0.75
Ti: Average	0.20	0.18	0.15	0.16	0.16	0.22	0.24	0.16
SD	±0.18	±0.12	±0.09	±0.07	±0.11	±0.13	±0.11	±0.10
Cr: Average	0.0119**	0.0122**	0.0137**	0.0473**	0.0147**	0.0154**	0.0394*	0.0157**
SD	±0.0067	±0.0042	±0.0089	±0.0320	±0.0063	±0.0015	±0.0201	±0.0106
Mn: Average	0.0081	0.0078**	0.0163**	0.0227**	0.0261**	0.0046**	0.0269**	0.0943**
SD	±0.0019	±0.0024	±0.0086	±0.0046	±0.0128	±0.0013	±0.0115	±0.0527
Fe: Average	1.84	3.41	2.50	1.63	0.71	0.96	3.35	5.86
SD	±1.67	±0.81	±1.39	±0.92	±0.46	±0.67	±2.23	±2.97
Cu: Average	2.75	2.56	23.14	2.77	0.88	0.36	13.02	0.0226**
SD	±2.37	±0.61	±11.24	±1.43	±0.76	±0.22	±1.02	±0.0090
Zn: Average	0.54	0.74	3.78	0.67	0.32	0.38	1.58	0.0174**
SD	±0.45	±0.57	±2.59	±0.58	±0.21	±0.16	±0.63	±0.0064

N/A* denotes the content of element is below the detection limit of EDS (<0.01 wt%) and can not be analyzed using PIXE.
** denotes the element is analyzed only by PIXE.

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