Jointly published by
Elsevier Science S. A., Lausanne and
Akadémiai Kiadó, Budapest

Journal of Radioanalytical and Nuclear Chemistry, Articles,
Vol. 192, No. 1 (1995) 147–154

ANALYSIS OF AN ANCIENT BRONZE STATUE BY EXTERNAL BEAM PIXE

N.B. KIM, D.K. KIM, H.W. CHOI, Y.S. KIM, H.J. WOO, K.S. PARK

Korea Institute of Geology, Mining and Materials,
30 Kajunmg-dong, Yusong-gu, Taejon,305-350, Korea

A quantitative analysis of an ancient Buddha statue was performed by external beam Proton Induced X-ray Emission for the purpose of identifying its originality. It is shown how the PIXE method can be applied for archeological study. The elemental composition of the statue is compared with that of several samples with definite ages. The experiment was performed by extracting 2.4 MeV proton beam through a 2 mm diameter collimator and 7.6 μm kapton foil to the He atmosphere. X-rays were measured by a Si(Li) detector. The analysed elements were Fe, Cu, Ag, Au and Hg for gold coating and Fe, Ni, Cu, Zn, As, Ag, Sn, Au, Pb and Bi for bronze body.

It is extremely helpful in archaeological study to know the composition of samples, since it allows us to classify the samples according to their ages and the places of production. PIXE (Proton Induced X-ray Emission) has often been applied to such analyses because of its inherent features such as nondestructive analysis, applicability to broad range of elemental concentration and fine local analysis. Inspired by these advantages, many archaeologists have applied PIXE analysis to various samples: coins[1], paintings[2], papers[3], prints[4] and potteries[5]. The external beam PIXE (Ext-PIXE) method has one more advantage over the conventional in-vacuum PIXE that even very large samples or samples which should not be damaged by vacuum can also be analysed. In spite of relatively large uncertainties in the analysis, the method is being used increasingly.

The classification of archaeological samples by elemental composition is usually done by discriminate diagrams[6] of composition of two or three elements. Samples of similar places or periods can usually be grouped on such a diagram apparently due to the similar material and manufacturing technique. By the statistical treatment of elemental composition for archaeological samples, one can establish a means through which the age and place of an unknown sample can be estimated.

0236-5731/95/US \$ 9.50

In this work, it is tried to identify the originality of a Buddha statue of unknown age by elemental anaysis. The Buddha statue is esteemed to be produced in the 7th century in the ancient nation of Unified Shilla. The central part of Unified Shilla was located in the southeast part of the Korean Peninsula. In this era, Buddhism was very prosperous and there remains many artistic Buddha statues produced by artisans.

The motivation was that archaeological markets are often flooded with forgeries which can hardly be distinguished from real ones only by outlook. If one had discriminate diagrams with good statistics, one could probably identify the originality easily. But since this approach has been stated just recently, we will just try to compare the composition of the statue with that of some proven real ones and with some proven forgery ones.

Experimental

External beam PIXE System: Fig. 1 shows the Ext-PIXE irradiation facility. The proton beam was produced by a 5 SDH-2 pelletron accelerator and was extracted through a 7.6 μm kapton foil window. Helium gas was supplied to the gap between the window, sample and the detector during the measurement in order to reduce the X-ray loss in the atmosphere. Beam size was restricted to 2 mm diameter and the external beam traversed 2.4 cm through the helium atmosphere. The detector was Canberra SL80175 Si(Li) with effective area of 80 mm^2 which showed a measured FWHM resolution of 195 eV at 5.895 keV. A 330 μm thick Myler funny X-ray filter with a hole

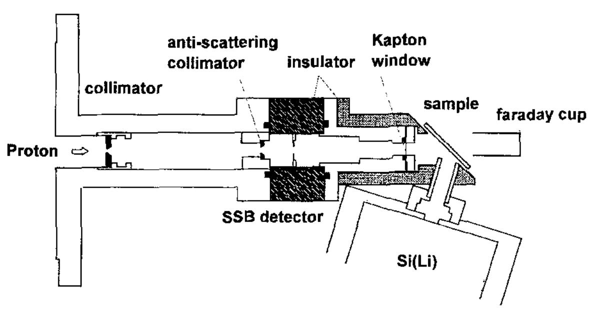

Fig. 1, Schematic diagram of the external PIXE beam line and target

of 0.4 % relative to the detector area was put in front of the detector. The target surface was kept always 45° to the beam in order to minimize the change of X-ray yields due to the geometry. The amount of proton irradiation was calculated by directly integrating the beam current collected on the

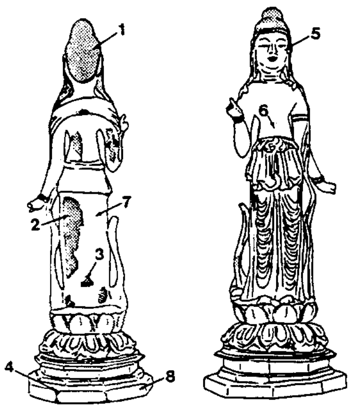

Fig. 2, Analyzed points of the Buddha statue.
The shadow parts indicated that the coating is peeled off (1-4: bornze, 5-8: gold).

target. The analysis point was adjusted by the laser light through the beam line.

Samples: The Buddha statue of unknown age is depicted in Fig. 2. The statue is 35 cm long and is made of bronze coated with gold. With age, some parts of the gold coating had been peeled off and weathered. Four points of coated gold and another four points in peeled-off parts (bronze parts) as selected in Fig. 2 were analyzed. Among 4 bronze points the point 3 has dark brown color while the others have blue-green color. The point was included in the analysis because one could suspect that the part around the point was repaired afterwards, even though gold coating remained in some of the part.

In order to compare the composition of the statue, the following reference samples were selected:

1) a bronze statue of the known era of 7th century,
2) a forgery gold coated bronze Buddha statue,
3) a 7th century gold coated earring and
4) a modern gold ring.

For these reference samples, at least two points were analysed. For the two buddha statues, exposed bronze and coated gold were analysed separately. In case of coated gold analysis, the elements composing the underlying bronze should not be detected. So the proton beam energy was adjusted to about 1.6 MeV - the maximum energy at which Sn peak from bronze did not show up in the X-ray spectrum. From the beam energy it was deduced that the coating thickness is about 8.4 μm. For the bronze and modern gold ring, 2.4 MeV proton beam was used.

Data processing: Signals from the Si(Li) detector were processed by means of a Canberra 2024 fast amplifier, a Canberra S-90 MCA and a MicroVAX II computer. X-ray spectra were analysed by the AXIL non-linear least squares fitting program[7]. Thin taget X-ray yields (counts/μC/μg cm^{-2}) for all the elements analysed were experimentally determined by relying on thin film standards available from Micromatter Company. In order to correct for the matrix effect of weathered materials it was assumed that the sum of these oxides was 100 %, and for non-weathered materials, sum of total elements was 100 %.

Results and discussion

Bronze: The X-ray spectra obtained from the unkown era Buddha statue, the 7th century one and the forgery one are shown in Fig. 3. The elemental concentrations of Fe, Ni, Cu, As, Ag, Sn, Au, Pb, and Bi are given in Table 1 with the data of a bronze sundial of the 15th century[8]. The elemental composition data lighter than Fe could be calculated by using funny filter at helium atmosphere but the analysis result can be largely deviated even by

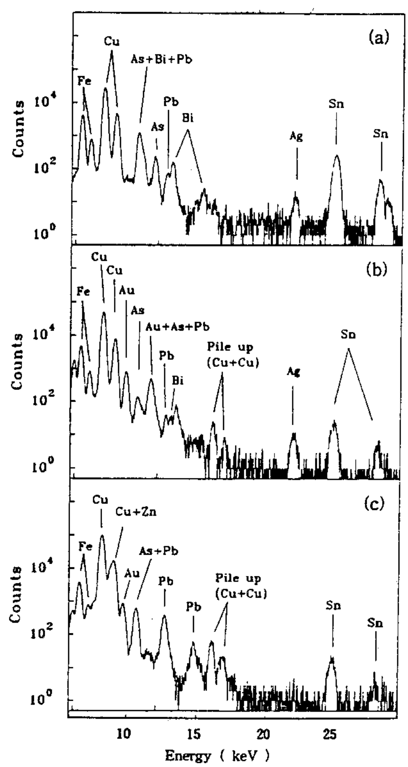

Fig. 3, X-ray spectra of bronze samples. (a) the unknown Buddha statue; (b) the 7c. statue; (c)the forgery statue small change in external beam condition, so omitted. The detected Ag and Au may be caused by the diffusion of coated gold.

On the first glance of Table 1, it can be seen that the point 3 has completely different composition from the others. This may lead to the conclusion that the part is reconstructed. A major feature of the unknown Buddha statue is the abnormally higher Sn content (more than 40 %) than normal (lower than 10 %)[9]. It is possible that the Sn content in the surface region is high because of the following reasons[10]: 1) With long time, the Cu on the surface oxidizes and is detached from the surface, resulting in the higher content of Sn compared with that in the body. 2) In the manufacturing

Table 1, Elemental concentration in bronze of each sample (unit: %). The uncertainty estimated is about 20 %.

Sample	Fe	Ni	Cu	Zn	As	Ag	Sn	Au	Pb	Bi
Unknown statue										
point 1	2.57	0.0841	32.9	-	2.25	0.399	41.8	0.306	0.399	1.66
point 2	3.76	0.0193	28.4	-	2.72	0.668	44.0	0.251	0.675	1.94
point 3	3.42	0.250	71.4	0.342	-	1.40	-	2.36	0.0484	-
point 4	1.46	0.0331	30.9	-	2.06	0.97	43.0	0.54	0.62	2.56
Avg. 1,2,4	2.60	0.0455	30.73	-	2.34	0.679	42.8	0.366	0.564	2.05
7 c. statue	3.31	0.418	48.1	-	0.257	0.747	5.91	6.09	0.403	0.465
15 c. sundial	0.31	-	65.	3.4	-	-	15.	-	4.9	-
Forgery statue	0.983	0.261	67.7	3.91	-	-	3.65	-	3.35	-

process Sn powder could often be applied on the surface before gold coating process to prevent the rapid oxidization of the surface. Therefore, the absolute content of Sn may not be valuable information as far as only the surface is analyzed. Rather, a more interesting feature is that it contains small amounts of As, Bi and Pb. It is noteworthy that it shares this feature with the 7 c. statue although the amounts show differences. It is known that small amounts of Zn, Pb and As were often deliberately added in the manufacturing process in order to lower the melting point and to finish the molding easily[11] even in the old days. On the other hand, As, Bi and Pb may be also just impurities existing in Sn because of their similar chemical properties. If they were impurities, the ratios between them would be a good measure to decide whether the used Sn ore originate from the same source. The As/Sn ratios are 0.055, 0.043, and 0 for the unknown, 7 c. and forgery, respectively. The Bi/Sn ratios are 0.048, 0.079 and 0. The Pb/Sn ratios are 0.013, 0.068 and 0.92. The ratios are quite similar between the unknown and the 7 c. one, but that of the forgery shows a remarkable deviation from the others. On the other hand Zn was detected only in the case of the forgery and the point 3 of the unknown. In summary, it seems that the Sn ores used in the bronze part of the unknown and 7 c. statues have the similar origin.

Gold: The X-ray spectra from the unknown Buddha statue, the gold coated earring and the forgery one are shown in Fig. 4. The elemental concentrations of Fe, Cu, Ag, Au and Hg in each gold coating are given in Table 2. About 20 % content of Hg was detected from the gold coating of each statue but not from the earring. This result indicates the difference in coating methods between them. The coating on bronze statues seems to be carried by the method of rubbing Au-Hg (or Au-Ag-Hg) amalgam to the surface which was a common Korean gold coating technique in the old days[10], and on earring by applying thin gold sheets on the frame. But the analytical results of gold coatings of the forgery and the unknown statue show no remarkable distinction within the error limit of the analysis. It is worthwhile to note Ag/Au ratios among the samples. The average Ag/Au ratio of the unknown and the forgery one are 0.013 and 0.024 respectively, whereas that of the 7 c. earring is 0.11. It is well known that about 10 % of Ag was added to increase the strength or to make a better color at that time.

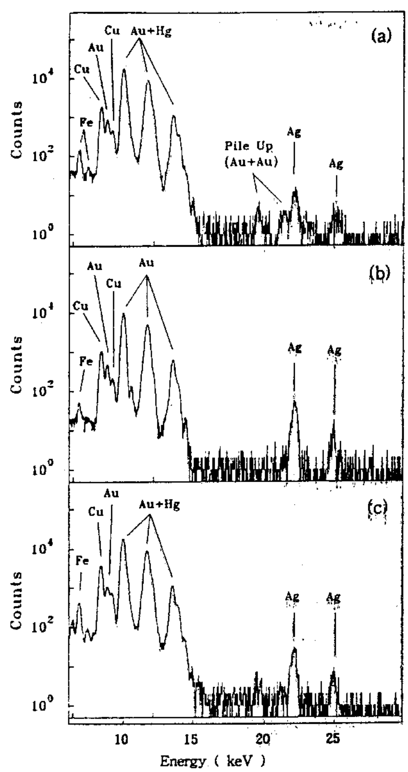

Fig. 4, X-ray spectra of gold coating. (a) the unknown Buddha statue; (b) the gold coated earring; (c) the forgery statue

Table 2, Elemental concentration in gold of each sample (unit: %).
The uncertainty estimated is about 20 %.

Samples	Fe	Cu	Ag	Au	Hg
Unknown statue					
point 5	0.0771	0.581	0.853	81.9	16.6
point 6	0.0702	1.36	1.27	73.5	23.8
point 7	0.0989	1.70	1.02	77.0	20.2
point 8	0.105	2.89	0.979	73.9	22.1
Avg.	0.0878	1.63	1.03	76.6	20.7
7 c. earring	0.0294	1.96	9.75	88.3	-
Modern ring	0.0792	0.0707	0.317	99.5	-
Forgery	0.265	3.28	1.79	73.9	20.7

From the analyses of bronze and gold parts, it may be deduced that the bronze body of the unknown statue may be original, dating about the 7th century except for the repaired part. But the gold coating seems to have been done only after the repair.

Conclusion

It has been shown that the Ext-PIXE method is very useful in archeological studies where the origin of a sample should be estimated. Also demonstrated is that by utilizing the nondestructive feature of Ext-PIXE even manufacturing methods may be reasonably deduced.

More complete information about the origin of an unknown sample may be possible if one construct a data base of elemental concentration with a large number of well known archaeological samples.

*

We would like to appreciate Dr. Dai Ill Kang in the National Research Institute of Cultural Properties for the kind advices and fruitful discussions. We also thank Mr. Boo Young Baek for providing the valuable ancient samples.

References

1. M.F.ARAUJO, A.C.ALVES, J.M.P.CABRAL, Nucl. Instr. Meth., B75 (1993) 450.
2. J.D.MACARTHUR, P.D.CARMINE, F.LUCARELL, P.A.MANDO, Nucl. Instr. Meth., B45 (1990) 315.
3. X.WU, X.Z.ZENG, F. YANG, Nucl. Instr. Meth., B75 (1993) 458.
4. T.A.CAHILL, B.KUSKO, R.N.SCHWAB, Nucl. Instr. Meth., 181 (1981) 205.
5. A.ZUCCHIATTI, H.J.ANNEGAN, M.A.KNEEN, C.VARALDO, Nucl. Instr. Meth., B75 (1993) 463.
6. J.MIRANDA, A.OLIVER, A.DACAL, J.L.RUVALCABA, F.Cruz, M.E.ORITZ, Nucl. Instr. Meth., B75 (1993) 454.

7. P.VAN ESPEN, H.NULLENS, F.ADAMS, Nucl. Instr. Meth., 142 (1977) 243.
8. N.B.KIM, K.S.PARK, H.J.WOO, H.W.CHOI, D.K.KIM, J.K.KIM, W.HONG, S.Y.CHO, Korea Institute of Geoldogy, Minidng and Materials Research Report, KR-92-2E-1, 1992, p.48.
9. W.D.CALLISTER Jr., "Materials Science and Engineering", John Wiley & Sons, New York, 1985, p263.
10. D.I.KANG, private communication.
11. D.C.JUNG, C.Y.YOO, H.S.HONG, H.T.KIM, "The Research of Traditional Science and Technology in Korea", National Science Museum, 1993.