

METALLOGRAPHIC AND LEAD ISOTOPE STUDIES ON METAL OBJECTS UNEARTHED IN THE TAK AREA, THAILAND

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I. Introduction

In September 1984 a vast number of Chinese and Thai ceramic wares suddenly appeared in the antique markets of Thailand. These artifacts were found to have come from the burial sites high in the mountains along the border of Thailand - Burma in Tak Province. During the months of September and October members of the staff of Chiang Mai University made expeditions to the area, and were able to obtain a representative collection of wares dug up, although most are broken pieces.¹ Since the diggings by the local people were uncontrolled and illegal, hardly any scientific archaeological excavation has ever been done.

Along with the Chinese and Thai ceramic wares an extraordinary group of white-glazed wares with green decorations was found. These wares were studied chemically by our group, and the results published in this *Journal*.² Judging from Chinese and Thai ceramics the date of the burial sites is supposed to be of the 14th - 16th centuries.

In addition to the ceramic wares a wide variety of iron and bronze artifacts was found including bronze lime pots and

bracelets. In this report metallographic studies on a bronze bell, bracelets and some other fragmentary relics are presented. Further, lead isotope ratios of these bronze relics are measured and the results are presented. The bell and the bracelet used for the studies are in the collection of Chiang Mai University. Other objects offered for our study are in private collections.

II. Metallographic Studies

Metallographic studies were carried out in the Sambo Copper Alloy Company.

1. Bracelet (Specimen 1)

(1) Appearance.

As shown in Fig. 1, the bracelet is covered with patinas. The diameter of the ring varies between 58 mm and 61 mm. The cross section of the wire is nearly oval. The values of the cross-sectional span measured at eight points are shown in Table 1.

Table 1. Cross-sectional span of the bracelet

	Maximal span	Minimal span
1	5.7 mm	4.8 mm
2	6.3	5.2
3	6.3	5.3
4	5.7	5.3
5	5.0	4.7
6	6.2	5.2
7	6.1	5.3
8	5.9	5.3

- (2) Specific gravity and weight.
The bracelet weighs 35.878 g and the specific gravity is 8.48, nearly the normal value of brass.
- (3) Hardness.
Approximately 10 mm was cut from an end of the bracelet. Vickers hardness (load: 5 kg) was measured at six points on the cross section. The values measured were 84.1, 77.9, 76.1, 85.7, 86.7 and 80.7, the average being 81.9.



Fig. 1. Bracelet (Sp. 1)

- (4) Chemical composition.
After removal of the patina on the surface of the specimen, quantitative chemical analysis of the metal was made. The results are shown in Table 2, together with the values of chemical analysis of the bell.

Table 2. Chemical composition of bracelet (Sp. 1) and bell (Sp. 2)

Element	Bracelet (1.1316 g)		Bell (0.0240 g)	
	Percentage	Method	Percentage	Method
Cu	77.9%	Titration	66.91%	ICP
Zn	Remainder	-	0.04	"
Sn	1.61	ICP	6.47	"
Pb	0.38	"	27.97	"
Fe	0.044	"	0.51	"
Ni	0.012	"	0.03	"
Mn	0.003	"	/	/
Al	<0.001	"	/	/
Sb	0.092	"	0.31	ICP
Bi	0.005	"	/	/
As	0.058	"	0.44	ICP
Ag	0.016	AA	0.058	"
Au	<0.01	"	<0.01	"
Si	0.023	ICP	/	/
Cr	0.002	"	/	/
Cd	0.001	"	/	/
Ti	0.001	"	/	/

ICP and AA stand for "Inductively Coupled Plasma Spectrochemical Analysis" and "Atomic Absorption Spectrometry," respectively.

- (5) Analysis by Electron Probe Microanalyser (EPMA).
The cross section of the specimen was observed. Fig. 2 shows the secondary electron image which reveals the recrystallized structures of brass. Figs. 3-6 show the X-ray images of copper, zinc, lead and sulfur, respectively, in which white regions indicate the presence of each element.



Fig. 2 Bracelet. Secondary electron image (X400)

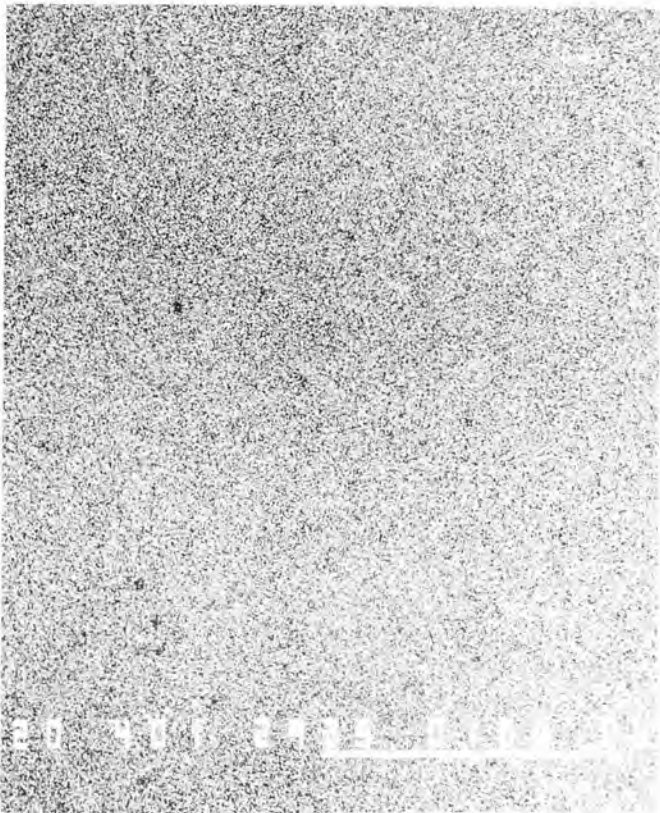


Fig. 3 Copper (X400)

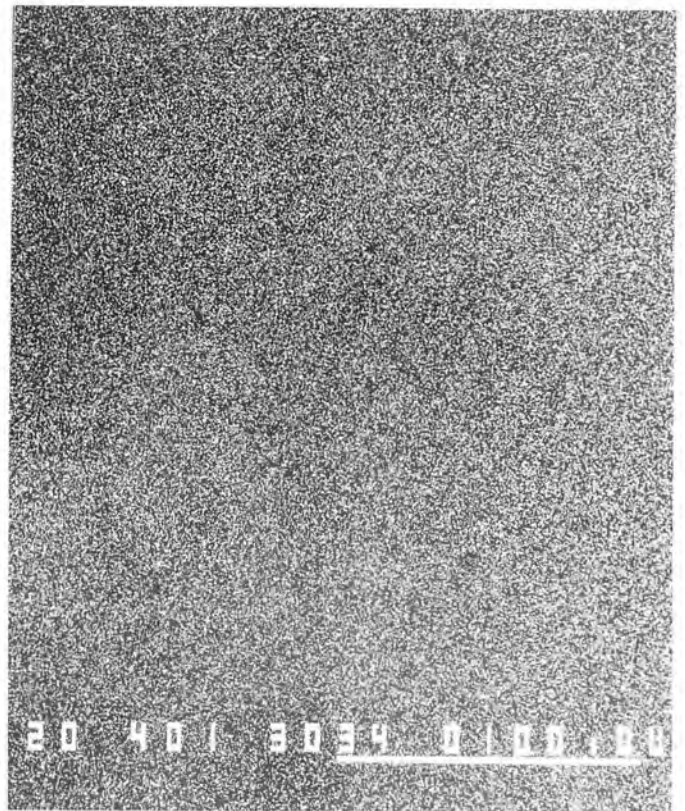


Fig. 4 Zinc (X400)



Fig. 5 Lead (X 400)



Fig. 6 Sulfur (X 400)

The observation of the structure hardly indicates any corrosion on the inside of the specimen. With large varying degrees of the recrystallized grain size, both fine and coarse grains are visible in a band form. The size of the coarse grains is approximately 0.09 mm, while that of the fine grains is approximately 0.045 mm. It is conceived that this is because of the varying degrees of fabrication in the forging process.

2. Bell (Specimen 2)

(1) Appearance.

As shown in Figs. 7 and 8 the bell is covered with green patinas containing copper ion. A part of the patina was peeled off and the texture in gray-white color is exposed. Also the presence of holes is visible in this section.

(2) Size and weight.

The diameter of the bell is 16.5-16 mm and is nearly spherical. The height is 23 mm. The outside and inside diameters of the ring are 11 mm and 5 mm, respectively, with the width 3 mm. A slit, with width 4 mm x 1.5 mm, is visible on the lower part of the bell. When shaken, the bell with a metal piece in it tinkles and it suggests that the degree of corrosion on the inside of the bell is not severe. The weight is 6.7063 g.



Fig. 7 Bell appearance (1)



Fig. 8 Bell appearance (2)

(3) Analysis by EPMA.

The analysis by EPMA was made on the cross section of a minute amount of the specimen taken from an edge of the slit. Figs. 9 and 10 show the composition images which reveal a slight degree of corrosion on the inside of the bell.



Fig. 9 Composition image (X150)



Fig. 10 Composition image (X400)

Figs. 11-16 show the X-ray images of copper, tin, lead, sulfur, iron and oxygen, respectively. In the figures white regions reveal the presence of these elements.

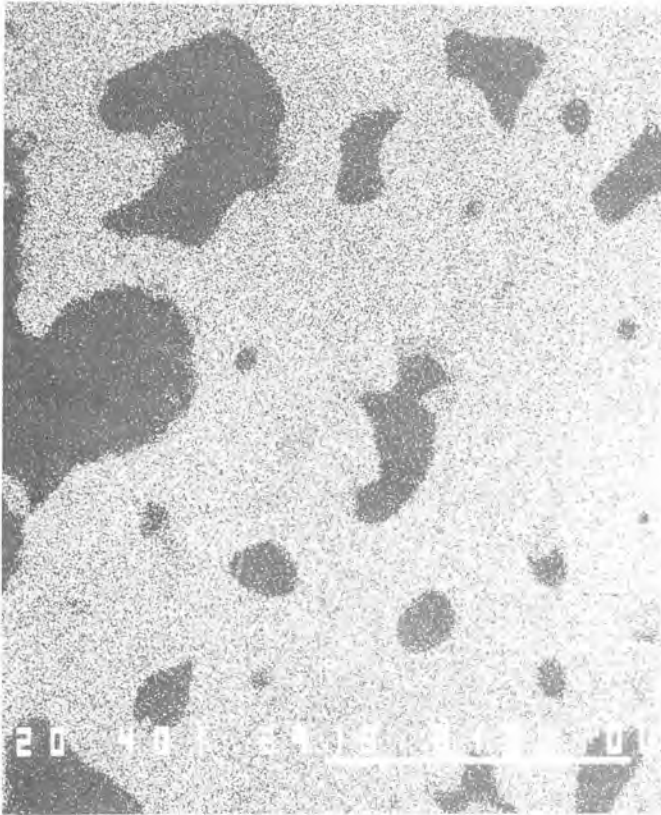


Fig. 11 Copper (X 400)

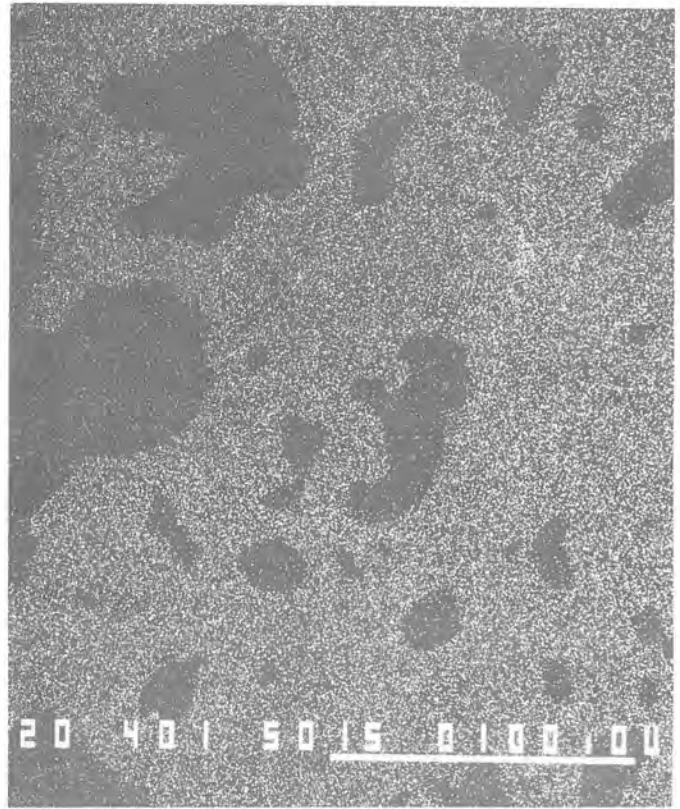


Fig. 12 Tin (X 400)



Fig. 13 Lead (X 400)



Fig. 14 Sulfur (X 400)



Fig. 15 Iron (X 400)



Fig. 16 Oxygen (X 400)

The composition images in Figs. 9-16 show that this is a cast structure and that the matrix is bronze consisting of copper and tin, with coarse white particles of lead. Black particles in Fig. 10 adjacent to the lead particles consist of copper (Fig. 11), sulfur (Fig. 14) and iron (Fig. 15) and it is conceived that these are the particles of chalcopyrite.

(4) Chemical composition.

The results of chemical analysis of the bell are shown in Table 2. The results for some elements were not available because of the minute amount of the sample.

3. Other Metal Objects

In addition to the bracelet and the bell studied above three other metal objects reportedly found in 1986 on a site in the Mae Sot area were examined.

(1) Appearance.

Specimen 3 is a triangular fragment (Fig. 17) 0.84-1.11 mm thick and its weight is 6.753 g. The chemical

composition is given in Table 3. It is a binary alloy of copper and tin, i.e. bronze.

Specimen 4 is a fragment of a wire and weighs 8.3966 g. It has the chemical composition shown in Table 3, and it is made of brass containing tin and lead (Fig. 18) which is close to gun metal in composition.

Specimen 5 is a fragment of a curved plate. The thickness at the outer rim is 1.6-1.9 mm and that of the inner rim is 0.8-0.95 mm (Fig. 19). It weighs 7.5292 g. Examination by EPMA revealed it as a bronze structure consisting of α phase and $\alpha+\delta$ phase with large lead particles scattered in them. Lead seems to have been obtained by smelting galena ores (Pb-Zn-S), and the Zn-S part seems to have remained in the lead particles. Thus this fragment is a ternary alloy of the Cu-Sn-Pb system.

(2) Chemical composition.

The chemical composition of Specimens 3, 4 and 5 analyzed after removal of patinas are given in Table 3.

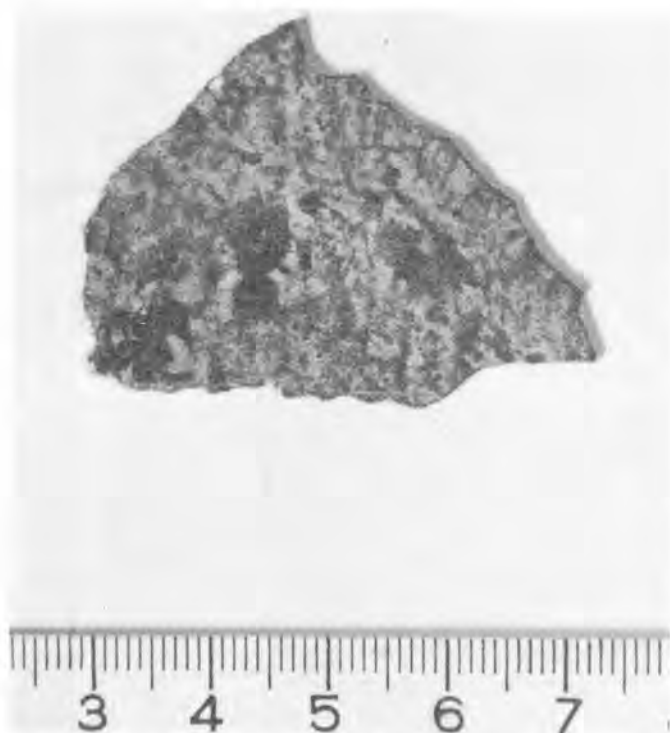


Fig. 17 Specimen 3. Triangular plate slightly corroded.



Fig. 18 Specimen 4. A wire fragment covered with green patinas.

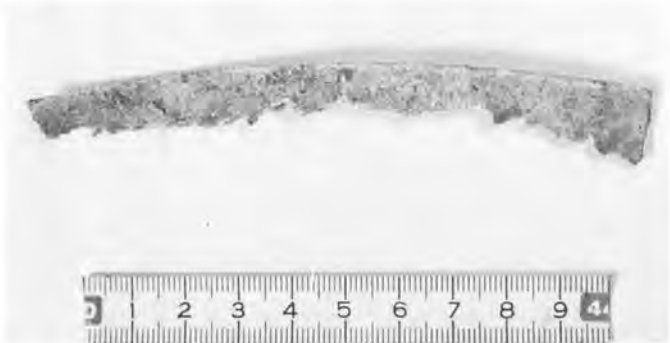


Fig. 19. Specimen 5. Curved plate fragment covered with patinas.

Table 3. Chemical composition of Specimens 3, 4 and 5

Element	Specimen 3 (1.851 g)	Specimen 4 (1.742 g)	Specimen 5 (1.742 g)	Analytical method
Cu	73.66%	83.09%	71.20%	Electrolysis
Pb	0.12	1.91	13.90	Electrolysis
Sn	23.03	3.00	9.80	Volumetry
Fe	0.14	0.02	0.16	ICP
Zn	0.02	11.56	2.18	ICP
Bi	0.014	0.007	0.087	ICP
Sb	0.14	0.055	0.16	ICP
Au	<0.001	<0.001	<0.001	AA
Ag	0.11	0.027	0.18	AA
Ni	0.12	0.004	0.053	ICP
Mn	0.003	0.006	0.002	ICP
Al	0.012	0.005	0.001	ICP
Cr	<0.001	<0.001	<0.001	ICP
Cd	0.002	0.001	0.005	ICP
Si	0.022	0.001	0.002	ICP
As	0.054	0.073	0.33	ICP
P	0.0092	0.0004	0.0022	Spectrophotometry
O ₂	0.65	0.040	1.10	Method by LECO
S	0.11	0.01	0.28	Method by LECO
Total	98.22%	99.81%	99.44%	

III. Lead Isotope Studies

Lead isotope studies were carried out using a mass spectrometer in the Muroran Institute of Technology, Muroran, Hokkaido, Japan.³

1. Method.

Since the first work of Brill⁴ in 1967 lead-isotope ratio determination has been used to study the provenance of various archaeological objects containing lead. By comparing lead isotope ratios extracted from metal objects with those of galena ores of various areas, it is often possible to decide the place where the objects might have been made. There is obviously a limitation that galena ores from different areas occasionally overlap in showing similar isotope ratios. The important advantage, however, is that only very small samples are consumed, and the isotope ratios are insensitive to the chemical forms of the samples; that is, even small amounts of patinas are useful for studies of bronze objects. Two of the present authors, M.M. and K.Y., have been applying this method to the study of archaeological materials such as glass and bronze excavated in Japan and China.⁵ In the present report the results on the metal objects found in the Tak area are presented.

2. Samples

In addition to the objects studied above, i.e. Specimens 1 (bracelet), 2 (bell), 3 (triangular fragment), 4 (wire) and 5 (curved plate fragment), two metal objects, Specimen 6 (bracelet) and Specimen 7 (lime pot) which were offered to us by Dr. John Shaw were examined. These two specimens were unearthed in the Tak area. They are shown in Fig. 20. This bracelet (Specimen 6) is quite similar in size and appearance to the other bracelet (Specimen 1), the diameter being about 6 cm. In Fig. 20 the lime pot is shown with its cap removed. The samples for lead isotope determination were taken from the surface of the bracelet (Specimen 6) and the inside surface of the cap of the lime pot to avoid contamination from outside. In both cases small amounts of green patinas were scraped off with a steel knife and used for mass spectrometry.



Fig. 20. Specimens 6 and 7 (bracelet and lime pot).

3. Results

The results of lead isotope determination of Specimens 1-7 and several galena ores are shown in Table 4. The galena ores used for determination are the same as reported in the previous paper.² In Fig. 21 the isotope ratio Pb 208/Pb206 is plotted against the ratio Pb 207/Pb 206 in accordance with the previous studies in this field.⁵

Table 4. Lead isotope ratios (metal specimens and galena ores)

Sample	Pb 206/Pb 204	Pb 207/Pb 204	Pb 208/Pb 204	Pb 207/Pb 206	Pb 208/Pb 206
Sp. 1 (bracelet)	18.36	15.56	38.56	0.8474	2.096
Sp. 2 (bell)	18.18	15.53	38.47	0.8541	2.118
Sp. 3 (plate)	18.38	15.67	38.67	0.8534	2.101
Sp. 4 (wire)	18.18	15.57	38.42	0.8617	2.111
Sp. 5 (curved plate)	18.26	15.61	38.62	0.8548	2.116
Sp. 6 (bracelet)	18.39	15.90	38.98	0.8647	2.121
Sp. 7 (lime pot)	18.13	15.38	37.99	0.8489	2.098
Galena, 1 Lamphun	18.26	15.76	38.65	0.8654	2.118
Galena, 2 Mae Hong Son	18.32	15.78	38.72	0.8615	2.115
Galena, 3 Mae Taeng	18.61	15.75	39.05	0.8458	2.097
Galena, 4 Hatyai	18.75	15.75	39.19	0.8394	2.091
Galena, 5 Mergui	18.73	15.72	39.29	0.8391	2.098
Galena, 6 Tenasserim	18.52	15.57	38.67	0.8402	2.089

The coefficients of variation of the ratios Pb 207/Pb 206 and Pb 208/Pb 206 are $\pm 0.2\%$ and those of the other three ratios are $\pm 0.4\%$, respectively.

The determined isotope ratios are divided into four groups, A, B, C and D. To Group A belong Specimens 4 and 6 and two galena ores, Lamphun and Mae Hong Son. To Group B belong Specimens 2, 3 and 5. To Group C belong Specimens

1 and 7 and the galena ore from Mae Taeng, and finally three galena ores from the Malay Peninsula, Hatyai, Mergui and Tenasserim, make up Group D. No specimen of metal belonging to Group D has so far been found.

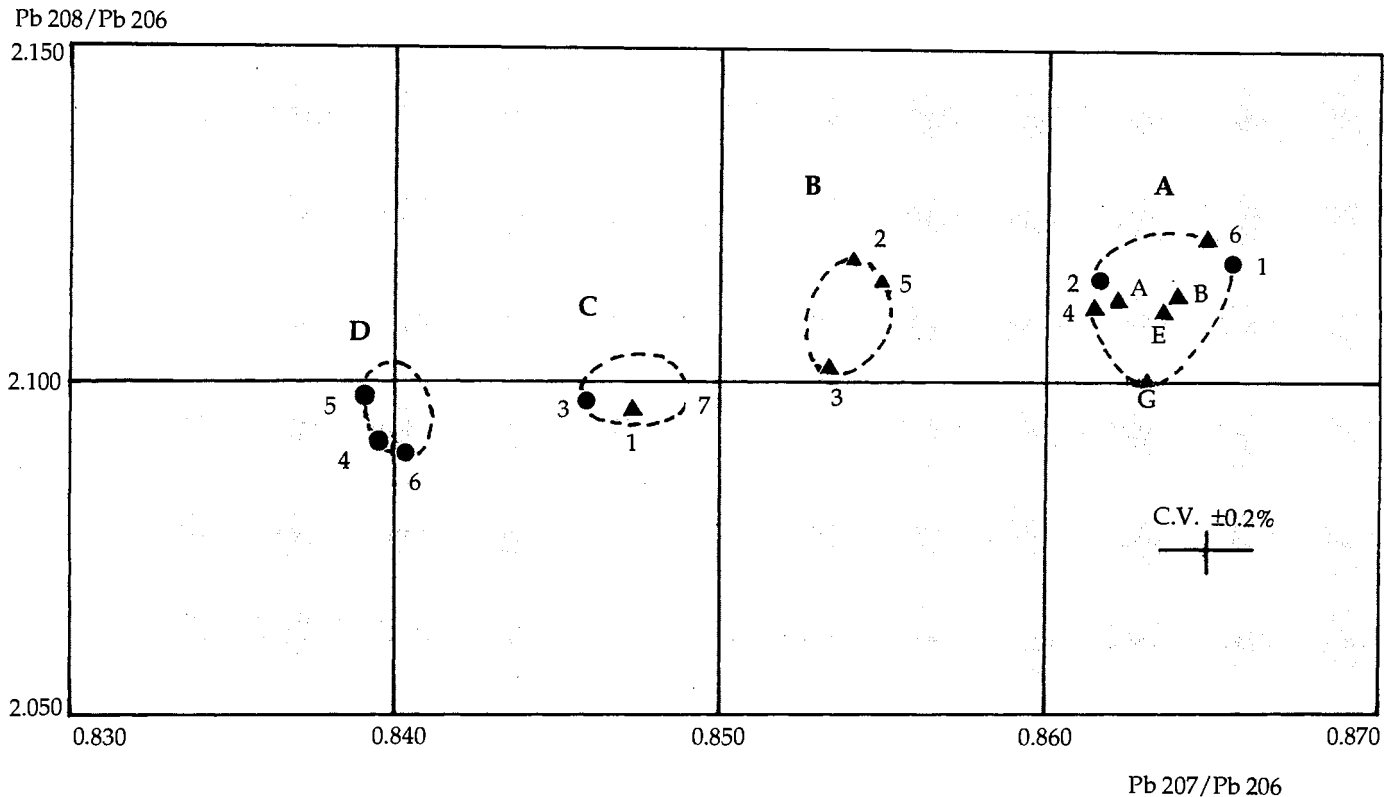


Fig. 21 Lead isotope ratios for relics and galena ores.

The symbols ▲ A, B, E and G, ▲ 1-7, and ● 1-6 stand for the objects reported previously (ref. 2), the metal objects in Table 4, and the galena ores in Table 4, respectively. C.V. means the coefficient of variation.

IV. Discussion

In the previous paper² lead isotope ratios were reported for three white-glazed wares and one plaque, and all these values are plotted again in Fig. 21 together with those of metal relics. The previous enter into the same Group A with two metal relics, bracelet and wire. In addition to these data there are unpublished isotope ratios measured for four plaques, one white-glazed plate with green decorations found in the Tak area, and two glazed sherds found in Pagan, Burma, all of which enter in Group A. As was discussed previously² large plaques decorated with two figures having animal heads and human bodies are supposed to have come from a temple near Pegu, Burma. These facts indicate that all the plaques, glazed wares, glazed sherds and metal relics belonging to Group A are made by using

the same lead ore produced in Burma, because the large plaques must have been made in kilns near Pegu which have not yet been found. This supposition seems plausible, although no lead ore produced in central Burma has been studied for its lead isotope ratios and the values have not been compared with those of the unearthed objects in the Tak area.

According to Mrs. Pailin Rerkjirasawad, who supplied the lead ore from 'Mae Hong Son,' this ore is believed to have come from Burma, because the place is close to the Burmese border and there is no lead mine in the Mae Hong Son Province. If this is true, the data for the 'Mae Hong Son' ore may represent lead ores in central part of Burma, and it is highly probable that all the relics in Group A were made in Burma.

For Group B there are two more unpublished examples of green-glazed pots, but no lead ore corresponding to this group is found, and no information on the provenance of the metal relics, bell, triangular plate and curved plate has been obtained. For Group C another example of lime pot has been found which has the same size and shape as the one studied above (Specimen 7).⁶ To this group belongs the lead ore from Mae Taeng, and its isotope ratios are different from those of the ores from Lamphun and Mae Hong Son. For Group D, which is represented by three lead ores in the Malay Peninsula, neither glazed wares nor metal relics have so far been found.

At the present moment it is difficult to find the place of production for the relics studied. The presence, however, of

three Groups, A, B and C, clearly indicates three kinds of lead ores were used for making these relics which were found in the border between Thailand and Burma. One of them, Group A, seems to be highly probably of Burmese origin.

As shown in Tables 2 and 3 the bracelet and the wire fragment are made of brass, whereas the other three metal relics are of bronze. It is interesting that brass was used for making metal objects in the 14th-16th centuries. As lime pots are related to the special custom of chewing betel nuts in countries like Thailand, Burma and Vietnam, the place of production of lime pots may be limited. Further studies on more samples of relics are needed.

ACKNOWLEDGEMENTS

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3. The lead isotope ratios were determined by a Hitachi RMU-6 mass spectrometer using a rhenium filament as the surface ionization device. The accuracy of determination was checked by using the standard sample, SRM 981, prepared by the U.S. Bureau of Standards. The metal objects were dissolved in nitric acid and lead was extracted by the dithizone method in a so-called clean laboratory. Lead was loaded on the rhenium filament with phosphoric acid and silica gel as stabilizers. The measured results were recorded and calculated by a computer.
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6. Two lime pots obtained separately show similar lead isotope ratios, whereas two bracelets show different values, one belonging to Group A and the other to Group C. The reason is not clear.