

## XVII. THE METAL ARTEFACTS

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### Introduction

**M**ETAL at Nong Nor was found predominantly as jewellery. Field identifications indicated that bronze bangles were by far the most common items. Notable exceptions were two caches of socketed copper implements, possibly arrowheads or chisels, and several tin artefacts, including bangles and a single earring. Bronze was also used in the repair of broken stone bangles, as has been observed at Ban Na Di (Maddin and Weng 1984).

More detailed analysis of the metals was undertaken in order to address the following questions:

- How many different metals and/or alloys were being used at Nong Nor?
- Tin artefacts have not previously been identified in Thai Bronze Age contexts. Can we confirm the field identification?
- Socketed copper arrowheads/chisels of a similar form also occur at Non Pa Wai, to the north (Pigott and Natapintu 1988). Do the Nong Nor examples also contain only copper; do they contain arsenic as a hardening agent?
- Lead is often used in Iron Age bronzes to assist in the casting of complex forms. Was lead a component of the Nong Nor alloys?
- Because the chemistry of the artefacts has been significantly altered, due to prolonged contact with ground water, it is important to clarify the relationship between the corroded and original metals.

Despite an intensive search using all the available techniques, particularly reflected light microscopy, only six out of nineteen samples investigated yielded metal and/or alloy phases. A number of the heavily corroded samples without any metal phase were also analysed to identify the secondary phases present and hence attempt to determine the original metal or alloy composition.

### Samples

A comprehensive study of all the metal artefacts was not feasible. Samples were taken from as wide a variety of artefacts as possible.

### Techniques

For the artefacts containing remnants of the original metal, polished samples were examined with

TABLE 33. *The analysed metal artefacts*

Cat. No.	Context	Description	Metal Phase Present	Analyses
38	B7	bronze bangle	no	XRF-TE
117	X1 L2:1	bronze bangle	no	XRF-TE
204 & 1104	B 25, area of	bronze bangle	no	XRF-TE
227	B 43	bronze pendant	no	XRF-p
528	B 97, area of	sheet bronze, pendant?	no	XRF-p
550	B 86	tin spiral bangle	no	XRF-up
551	B 86	tin spiral bangle	no	XRF-up, EMPA
552	B 89 pot, area of	bronze pendant, bell?	no	XRF-p
556a	B 102	copper arrowhead, socket	yes	XRF-TE, XRF-p, EMPA/
556b	B 102	copper arrowhead, socket	no	XRF-TE
556c	B 102	copper arrowhead, blade	yes	XRF-p, EMPA, element map
604	B 105	bronze bangle	yes	XRF-p, EMPA, element map
671	B 112	bronze bangle	yes	XRF-up, EMPA
882	B 147 (pot), in fill of, B 138	bronze strip, at rim of pot	yes	XRF-p, EMPA, element map
964	B 147, adjacent	bronze bangle	no	XRF-p
967	B 147, adjacent	bronze bangle	no	XRF-p
1096	B 111	bronze bangle	no	XRF-p
1097	B 35	bronze bangle	yes	XRF-p, EMPA, element map
1190	B 49	tin bangle/ring	no	XRF-p, EMPA, element map

TE: Trace Element, p: polished artefact, up: unpolished artefact

a reflected light microscope and chemically analysed with a Jeol JX 8600 electron microprobe (EMPA) following techniques developed by Nakamura and Coombs (1973). Mineral identification was by X-ray diffraction (XRD) using a Phillips PW1010 diffractometer with identification based on the search programme MacDiff. Bulk samples of the oxidised artefacts were scanned using X-ray fluorescence analysis (XRF, Phillips PW 2400) to determine the element content qualitatively.

#### Petrography of the metals

The metals copper, tin and a bronze alloy have been identified in a limited number of samples. Reflected light microscopy reveals significant differences between the bronze samples and the

unalloyed metals. The copper and tin have an equigranular texture typical of equilibrium crystallisation, with individual crystals being about 0.14-0.25 mm in diameter. In contrast, the bronze samples show the classic dendritic pattern of quickly cooled metals with individual dendrites being up to 0.4 mm long. In the case of bronze in cat. 1097, rectangular exsolution features at the 100 micron scale can also be observed (Fig. 99).

### Chemistry of the metals

Because the amount of metal present is small, all samples were analysed by EMPA. This technique analyses small volumes of a few cubic micrometres. The EMPA analysis is dependant on analysing a flat polished surface which was difficult to achieve because of the corroded nature of the samples. As a result many of the analytical totals show some minor variation around 100 per cent.

Anomalous readings also resulted from measuring areas where the original metal had corroded to an oxide, hydroxide or carbonate. For example, one reading on cat. 556c, a copper artefact, gave 56.33 per cent copper with no other metals present, indicating that in the area analysed copper metal had corroded to  $\text{CuCO}_3\text{Cu}(\text{OH})_2$  (malachite) which has 56.97 per cent copper. Such readings were easily identified and discounted.

### Copper

Remnants of copper metal have been found in three samples cat. 882, cat. 556a and cat. 556c. Most of the metal has been oxidised to the copper oxide, cuprite. There are trace concentrations of tin in cat. 882, with a maximum concentration of 0.56 per cent, which is close to the minimum detection limit and probably means that no tin is present in this sample.

### Bronze

In the bronzes, discounting readings on corroded metal, variation in the ratio of copper to tin at different points on the same sample was evident. This variation can be the result of several processes including; original inhomogeneities in the metal, re-equilibration following casting, mechanical displacement and/or oxidation during high temperature working, oxidation during corrosion and exsolution (Charles 1973). In table 34, copper/tin ratios are therefore given as a range rather than in absolute terms. An average composition of 7-10 per cent tin is indicated.

TABLE 34. *Microprobe analysis of bronzes*

Context	Sample made up of:	Measured metal Cu:Sn	Cu/Sn ratio	Probable original composition Cu:Sn
cat. 604 B 105 bangle	bronze metal, oxides & carbonates of tin & copper	91.6:12.4	7.36	88:12
cat. 671 B 112 bangle	bronze metal, oxides & carbonates of tin & copper	88.0:12.6 88.1:9.7 93.4:6.3	14.95 9.02 7.01	87:13 90:10 94:6

TABLE 34 (cont.). Microprobe analysis of bronzes

Context	Sample made up of:	Measured metal Cu:Sn	Cu/Sn ratio	Probable original composition Cu:Sn
cat. 1097	bronze metal, oxides	85.4:14.3	5.6	86:14
B 35	& carbonates of tin	<b>94.3:6.8</b>	<b>13.9</b>	<b>93:7*</b>
bangle	& copper	98.2:5.6	17.5	95:5

\* indicates a reading representative of many taken on this sample. The two other readings are at the extremes of the range observed

## THE OXIDISED ARTEFACTS

### Mineralogy of the oxidised artefacts

The majority of the artefacts are extensively corroded through reaction with oxygenated ground water which has converted the original copper alloys to a variety of minerals. Optical examination of samples suggests that cuprite ( $\text{Cu}_2\text{O}$ ) and malachite ( $\text{CuCO}_3\text{Cu}(\text{OH})_2$ ) are the major minerals present in the artefacts. This has been confirmed by XRD analysis and is illustrated in figure 97 where the only phases present are the copper oxide (cuprite) and the copper carbonate hydroxide (malachite). Other minerals include azurite and the tin oxide romarchite. From this mineral assemblage, it is possible to predict from geochemical calculation the conditions under which the artefacts were oxidised. Cuprite and malachite are only stable at a pH of greater than eight and an Eh of *c.* + 0.15, so alkaline oxidising conditions are indicated.

Only one of the oxidised bronze samples contains any tin-bearing phases; romarchite ( $\text{SnO}$ ) has been identified as the major phase coexisting with quartz. The limited presence of tin-bearing mineral phases is unusual given that the samples appear to have been bronzes. In an attempt to identify such phases, a sample was investigated using element mapping techniques on the electron microprobe confirming the dominance of copper carbonates and copper oxides (Fig. 98). Two analyses of five micrometre areas of higher tin concentration on a sample from cat. 38 showed 31 per cent and 42 per cent tin respectively. These high tin concentrations are probably the result of copper being lost from the sample. It should be noted that this high tin mineral phase has yet to be identified.

### Petrography of the oxidised artefacts

Petrographically the oxidised bronze artefacts show textures reminiscent of dendritic growth (Fig. 99). The comparison with textures of modern bronze alloys is difficult to make since the major oxidation phase present is the deep red copper oxide cuprite whose depth of colour tends to obscure detail and makes petrographic examination difficult. In addition, the alteration and crystallisation of cuprite from the copper alloy together with the *in situ* crystallisation of other secondary minerals such as malachite, azurite and romarchite may have had a significant modifying effect on the textures in the sample. Hence the present textures may not be original.



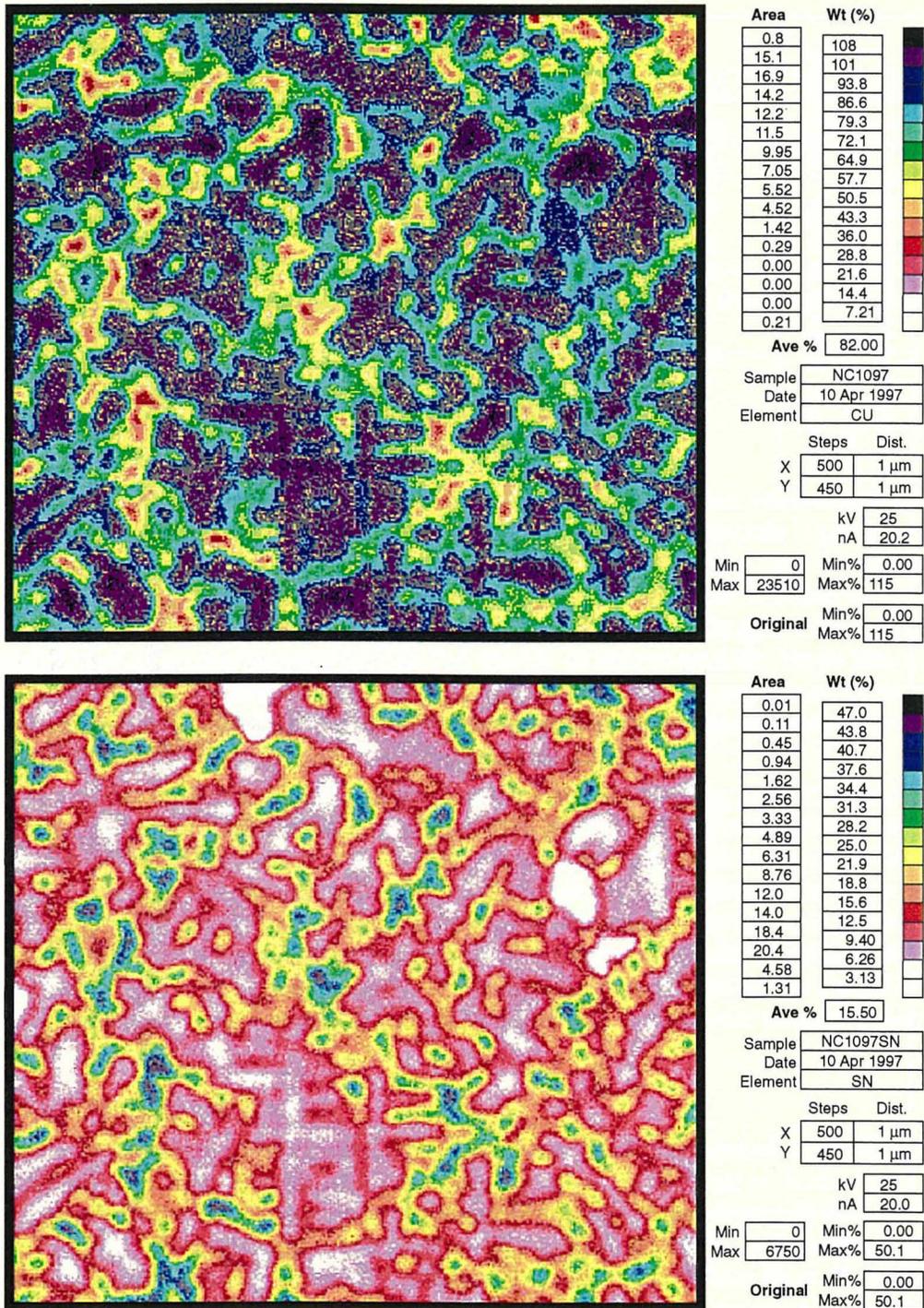


FIG. 98. Element maps for copper (*above*) and tin (*below*) over a 500 x 450 μm area of cat. 1097. Dendritic structure is indicated by the angular textures in the lower central portions of the maps

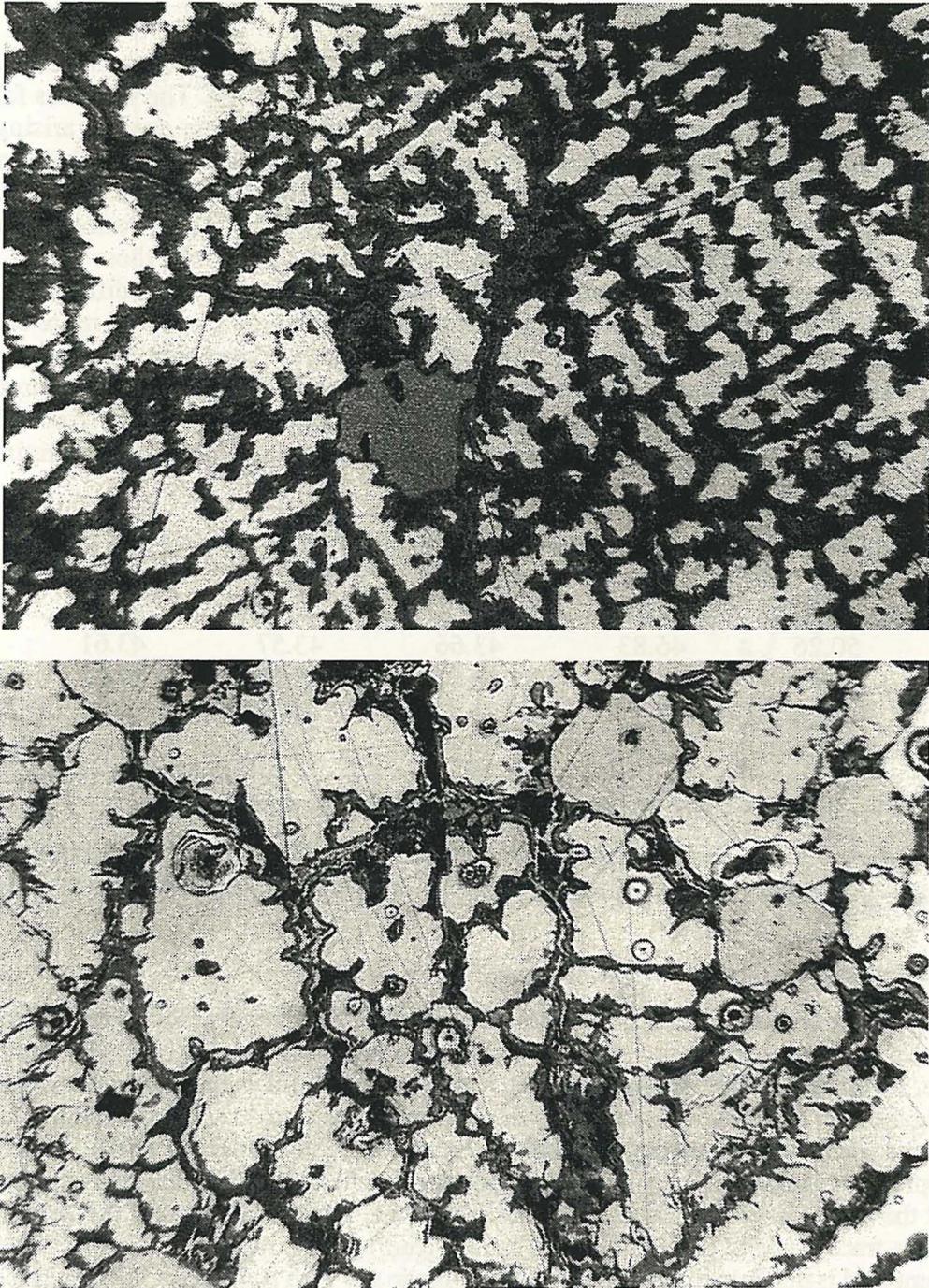


FIG. 99. Polished sections of cat. 1097 (*above*) and cat. 671 (*below*) showing dendritic structures. Three slightly darker grey sub-circular features in top right of cat. 671 micrograph are composed of copper (magnification =  $\times 165$ )

### Chemistry of the oxidised artefacts

The chemistry of all the oxidised samples is dominated by copper and/or tin. Analyses of three oxidised bronze samples are given in table 35 recalculated to oxides. The analyses fall short of 100 per cent and the difference will be due to carbon dioxide and water content arising from the oxide and carbonate phases present. Copper/tin ratios in the samples are also given in table 35. The three samples analysed sort into two groups based on copper/tin ratios; cat. 38 with a Cu/Sn value of *c.* 4.4, and cats. 117 and 204 with an average value of 2.7. These ratios would indicate bronzes with 18 and 27 per cent tin respectively. However, it is likely that these values have little relevance to the original composition of the metal since copper and tin have different chemistries and will behave differently in the oxidising ground water situation. Copper is more soluble than tin in the mildly oxidising situation and it is probable that the copper/tin ratio changed during oxidation, in which case the ratio is likely to have decreased. The ratios observed in the bronze metals vary between 6.1 and 19 (Cu/Sn) indicating that copper has been lost from the oxidised samples. This is consistent with the oxidised and metallic archaeological samples originally being of similar composition.

Table 35. *Bulk major element analyses (weight per cent) of oxidised samples*

Cat. No.	38a	38b	117a	117b	117c	204
Cu	50.26	46.83	43.66	43.57	43.61	42.99
Sn	11.82	10.63	15.47	16.25	17.21	16.16
Fe	1.16	1.12	0.36	0.98	0.31	0.70
Cu/Sn	4.3	4.4	2.8	2.7	2.5	2.7

38a & b and 117a, b & c refer to multiple samples prepared from just two artefacts

Analyses of cats. 551 and 1190 do not show any copper content. The original artefact must have been composed of unalloyed tin but all the original metal has been converted to tin oxides and/or carbonates.

### Trace element content of the oxidised artefacts

Trace elements can provide evidence for the origin of the ores smelted to produce the bronze, copper or tin artefacts. None of the metal samples was available in sufficient quantity for an XRF scan, so as an alternative, a number of the oxidised samples were scanned. A trace element scan of one sample is given in figure 100. The only trace elements detected were titanium, iron, lead, vanadium and manganese. Titanium, iron and manganese are likely to be present in the hundreds to thousands of parts per million (ppm) concentration range whilst the other two elements will be in the tens of ppm range. It is likely that the oxidation and hydration process responsible for the corrosion of the artefacts has also modified the trace element content so little can be read into the results. However, in the oxidising environment lead is unlikely to migrate so it is possible to say with some certainty that lead contents of the original artefacts must have been in the few parts per million range. Seeley and Rajpitak (1984) have reported varying concentrations of lead, arsenic, antimony, iron, silver, nickel, cobalt, bismuth and zinc in samples from Ban Na Di. If any of these elements is present in the oxidised samples, then their concentration is likely to be less than 50 parts per million.

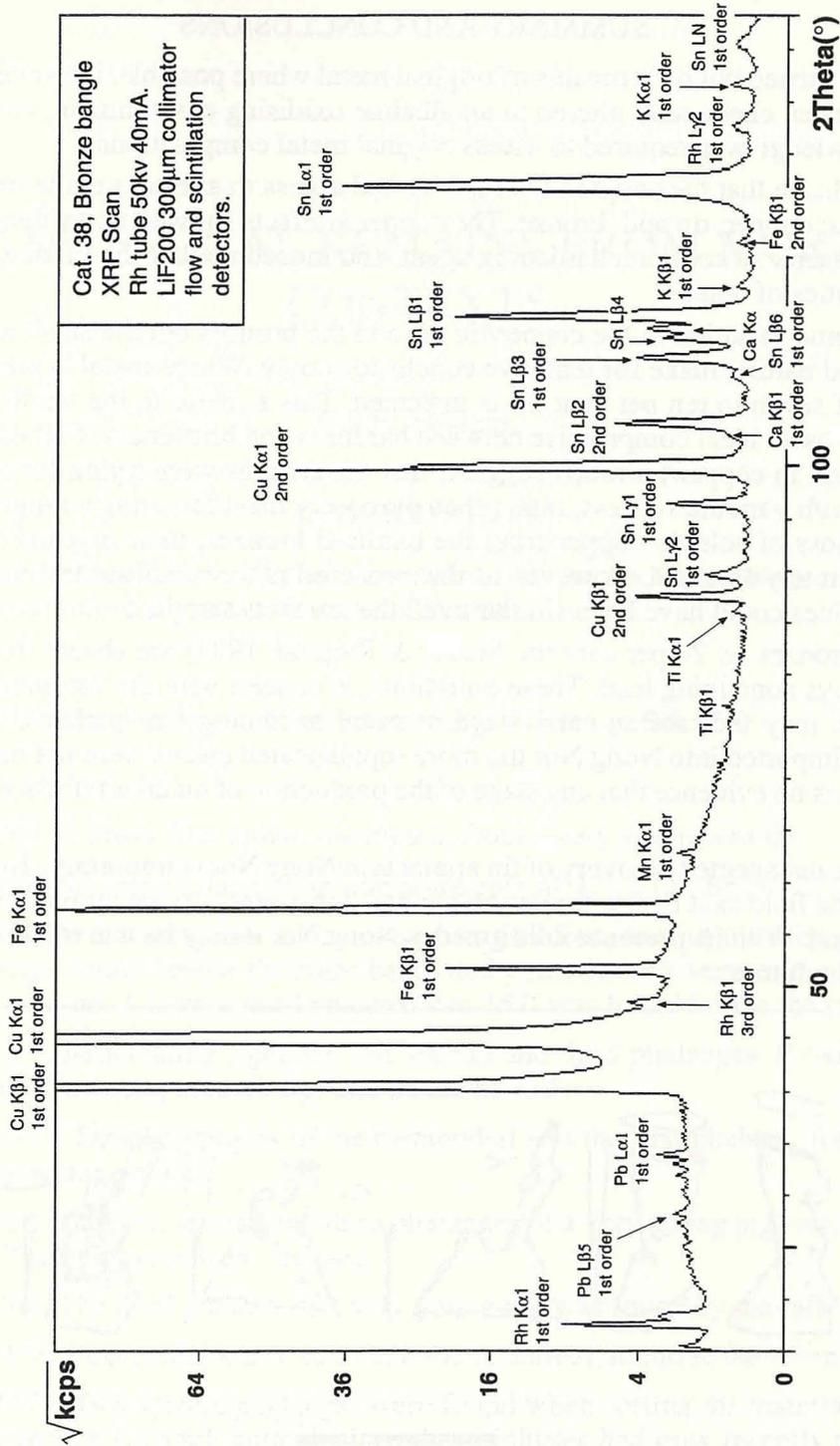


FIG. 100. XRF trace element scan of cat. 38. The x axis has been exaggerated by using  $\sqrt{\text{kcps}}$ , rather than kcps (thousand counts per second), to assist identification of trace elements.

## SUMMARY AND CONCLUSIONS

Analyses were carried out on remnants of original metal where possible. However, as most of the artefacts have been chemically altered in an alkaline oxidising environment, chemical and mineralogical knowledge was required to assess original metal compositions.

Results indicate that the people of Nong Nor had access to artefacts made from at least three different metals; copper, tin and bronze. The copper artefacts showed no evidence of significant inclusions of arsenic, a common hardening agent, and indeed neither the tin nor copper artefacts had any impurities of note.

There is some variation in the copper/tin ratio in the bronzes but the small sample analysed, and its corroded nature, make for tentative conclusions only. Where metal is present, an average composition of seven to ten per cent tin is indicated. This is close to the ten to twelve per cent range regarded as an ideal compromise between hardness and brittleness (Forbes 1964:146). The level of variation in copper/tin ratios suggests that the artisans were trying for a single standard composition, with variable success, rather than purposely manufacturing a range of metals. Due to a probable loss of soluble copper from the oxidised bronzes, their original copper/tin ratios cannot be accurately assessed. However, as the measured ratio values are less than in the metals, the original values could have been similar in all the artefacts sampled.

High-tin bronzes (c. 24 per cent tin; Seeley & Rajpitak 1984) are absent from Nong Nor, as are ternary alloys containing lead. These omissions, in concert with the variation in composition of the bronzes, may indicate an early stage in metal technology, or perhaps, that when metal artefacts were imported into Nong Nor the more sophisticated pieces were not made available. In any case, there is no evidence that any stage of the production of metal artefacts was carried out at Nong Nor.

Finally, the unexpected recovery of tin artefacts at Nong Nor is important. Tin is very difficult to identify in the field as it is of a similar colour and consistency to the alluvial deposits in which it has been found. With its presence confirmed at Nong Nor it may be that tin will be identified at more sites in the future.

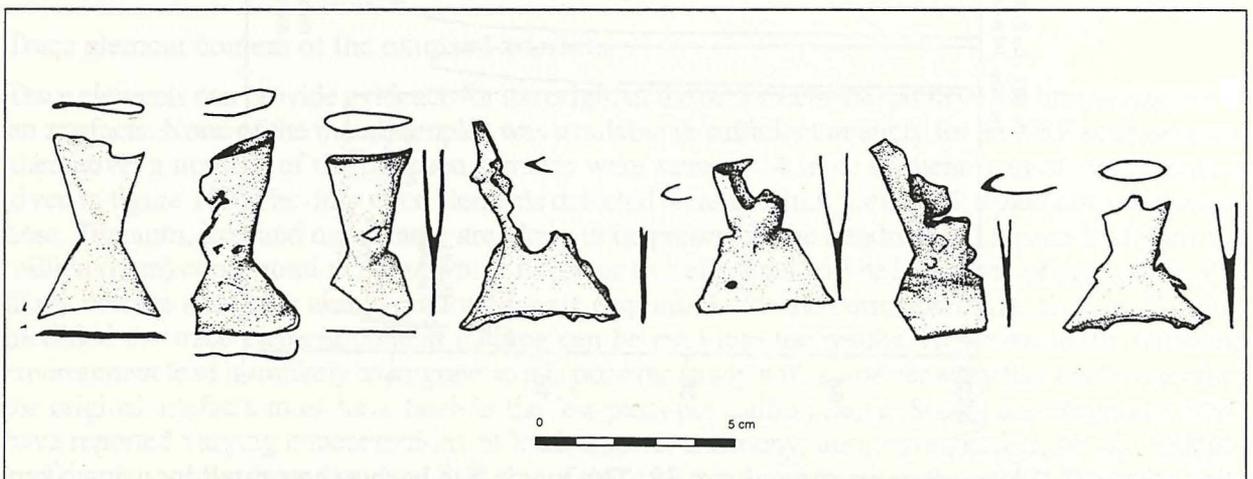


FIG. 101. Copper socketed artefacts, cat. 556, from burial 102