Appendix H

XRF Analysis of Mycenaean bronzes from the Menelaion

by R. E. Jones

In 1975 and 1977 the writer carried out a programme of non-destructive analysis by X-ray fluorescence spectrometry (XRF) of copper, bronze and other metal artefacts from the excavations at the Menelaion. This formed part of a broader enquiry in the 1970s and early 1980s by the writer and H.W. Catling into the alloying patterns in bronzes of the later prehistoric period and to a lesser extent in the Early Iron Age from sites mainly in the Peloponnese and Crete, some results of which have already been published.[1] Since that time, additional analyses have been made with similar aims of bronzes from Kallithea tombs in Achaea and the Citadel House, Mycenae, and of some of the well-known decorated bronzes from Mycenae, Prosymna, Dendra and Routsi (TABLE H.2). More specific aims of the programme were to look for possible correlations between composition and function or type of artefact, as well as to make comparison with chronologically and typologically similar bronzes on an inter-site and inter-regional basis. The evidence for metal working at the Menelaion is presented elsewhere in this volume.

At the time the analyses reported here were carried out, the corpus of composition data on prehistoric and later Greek bronzes was relatively limited. Since that time, the situation has altered considerably: the database has expanded as a variety of investigations have been made with different analytical techniques, some having similar, essentially technological aims to the present one,[2] others seeing composition data as a necessary preliminary to lead isotope analysis for information on copper sources.[3] The potential interest of the present study is that it formed part of a methodologically uniform project as outlined above, and crucially it exploited the unique advantages of the technique, that is, the instrument was taken to where the bronzes were stored. The analyses were rapid and non-destructive, and no sample was removed to a laboratory for analysis.

The results of analysis by the same method of the more numerous bronzes of post-Bronze Age date will be reported separately.

METHOD

The technique of analysis was XRF, using the so-called Isoprobe, developed at the Research Laboratory for Archaeology.[4] The instrument was transported easily by car from the Fitch Laboratory to the *apothiki* at Aphyssou where the analyses were made. An Americium 241 gamma-ray source was used to excite the fluorescence of elements having higher energies, such as tin and silver, while an X-ray source, operating at 15 KV, 0.7 mA) was used for all other elements; those lighter than potassium were not detected. The detector, manufactured by Princeton Gammatech, was of the intrinsic germanium type with a resolution of 170 eV. The 400 channel multi-channel analyser was normally preset to 2×10^4 counts for each sample analysis. Peak heights and background were measured from the spectrum displayed on the monitor. Semi-quantitative estimations of the tin, lead and arsenic contents were made with reference to calibrations (Cu/Sn peak intensity ratio vs. %Sn for each standard) prepared daily from six bronzes of known composition. Arsenic and lead, which fluoresce in the 10–11 KeV region, were distinguished in the XRF spectrum by determining the position of their secondary peaks which are well separated. Copper was estimated by difference. In the same way, silver (and copper) content in gold were determined from gold/electrum standards.[5]

The analytical procedure and performance characteristics of the method have been presented in some detail elsewhere; here it is necessary to highlight the following important points:

[1] Catling and Jones 1976; 1977; Rapp *et al.* 1978; Jones 1980; Jones 2008.

[2] Principally, Mangou and Ioannou 1999; Mangou and Ioannou 2002; Pare 2000

[3] See, for example, Gale and Stos-Gale 1982.

[4] Hall *et al.* 1973

[5] Jones R. E., 'Analyses of gold objects from Lefkandi', in M. R. Popham, L. H. Sackett and P. G. Themelis (eds.), *Lefkandi I: The Iron Age Cemeteries. The Cemeteries. BSA* Suppl. 11 (London 1980) 461–4.

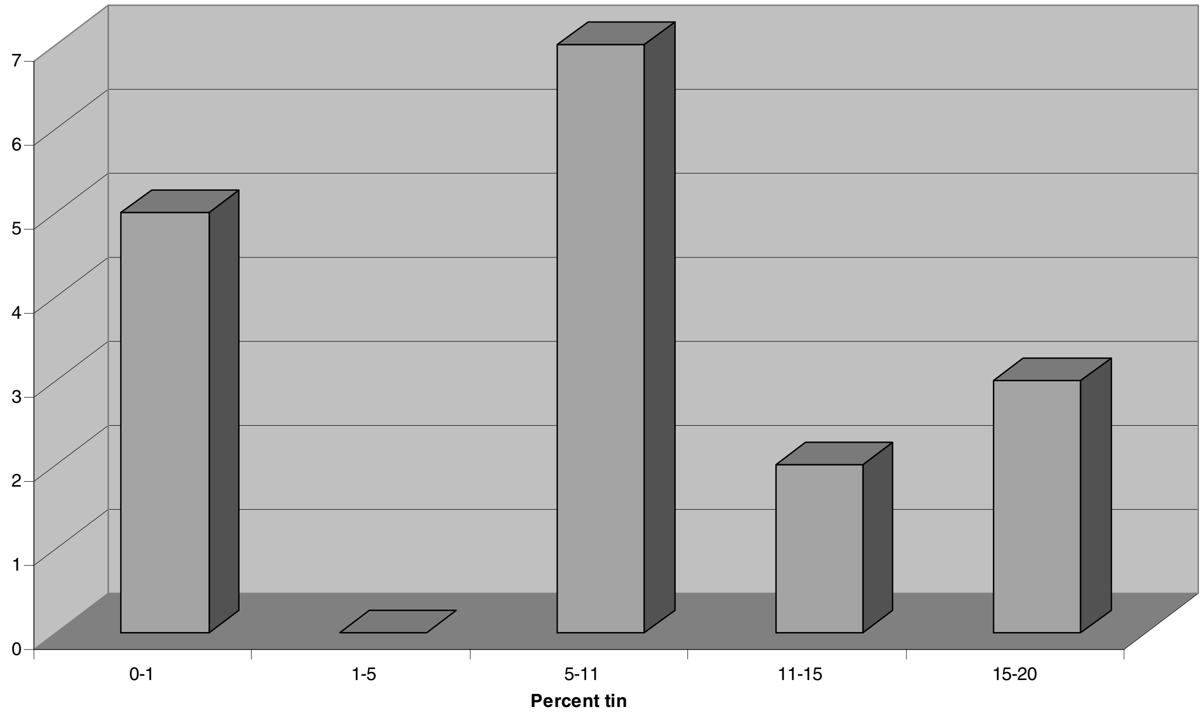

FIG. H.1. The distribution of tin content ranges in bronzes from the Menelaion.

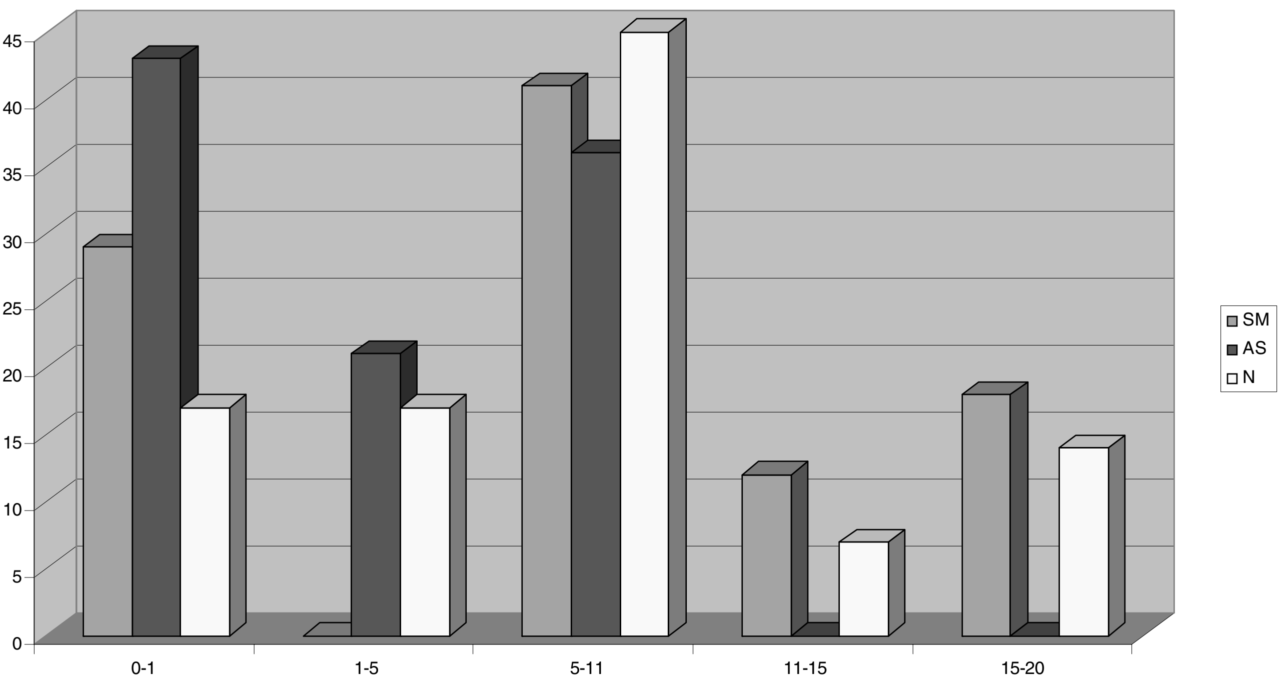

FIG. H.2. Percentage proportions of tin ranges in bronzes from the Menelaion (SM), Ayios Stephanos (AS) and Nichoria (N) analysed by XRF.

(a) Each artefact selected for analysis was examined under a stereomagnifier to locate one or more areas (usually a few square millimetres) on the surface that could, if required, be cleaned to provide a suitable target for analysis. The quality of the prepared surface, which in turn greatly affects the ability to provide a reliable estimation of the composition, was graded accordingly: **A** no corrosion (good metallic surface) to **E** heavy corrosion (green malachite patina predominating). The intermediate grade **C** represented a metal surface showing corrosion to the extent of a visible red or dark copper oxide layer. Replicate analyses were made on a majority of the bronzes.
(b) The detection limits for Sn, Fe, Zn, Ni, Pb and As were 0.5, 0.5, 1, 0.5, *c.* 0.5 and 1% respectively.
(c) Estimates of the performance characteristics of the analytical procedure were routinely made. The overall error in the determination of the tin content in the range 0–15% was not less than +/- 15% for A and B grade surfaces and not less than +/- 20% for C and D grade surfaces. Above 15% tin content and/or in the presence of more than 5% lead, the tin content estimation is given as a range. These are likely to be best estimates and do not take account of random errors introduced by, for example, fluctuating mains voltage occurring during analysis.[6] *As a result, the writer's more recent reports on analyses using the XRF system described here state that the analyses are semi-quantitative; this applies to the present analyses.*

Results

The seventeen bronzes selected for analysis (X% of the total number from the site) were those in reasonable condition and having recognisable identity. Their compositions (TABLE H.1) indicate that they are tin bronzes or copper; arsenic was not found above its detection limit.

TABLE 1. The compositions of Mycenaean copper, bronze and lead objects from the Menelaion, determined by XRF. For the copper and bronze objects, the percentage contents of tin and lead are given. Copper forms the remainder of the composition. Arsenic was not detected above its detection limit. tr = trace; pr = present.

Catalogue No.	*Description*	*Date*	*Scale*	*Sn*	*Pb*	*Au*	*Ag*
M3	Arrow-plate	LH IIIA1–B2	B	15–20			
M5	Arrow-plate	LH IIIA1	B	13			
M19	Graver or small chisel	LH IIIA	B	6	tr		
M24	?Large awl	LH IIIA1	B	10			
M28	Chip broken from heavy tool	LH IIIA1	C	11			
M57	Scrap	LH IIIA1–B2	B	15–20			
M36	Handle rivet	LH IIIA1	B				
M15	Saw fragment	LH IIIA1	A/B	9			
M20	Drill or graver	LH IIIA1	B	8			
M43	Tinker's patch	LH IIIA1	B				
M3	Arrowplate	LH IIIA1–B2	B	15–20			
M37	Handle rivet	LH IIIA1–B2	B	8			
M45	Mould strapping	Not later than LH IIIA1	A/B				
M17	?Drill	LH IIIA1	B	15			
M40	Ajoure fragment	LH IIIA1	B	9	tr		
M66	Waste (pellet)	LH IIIA1	B/C				
M63	Waste (nodule)	LH IIIA1	B/C				
SF4 LEAD	small spear head				pr		
M170	gold fragment					80	20

[6] This was a problem in rural areas of Greece in the 1970s and 1980s, especially between the hours of 8 am and 3 pm. Mains voltage was monitored during analysis but there were no practical means of smoothing the fluctuations.

There is a range of compositions from unalloyed copper to high tin bronzes (FIG. H.1). Into the former category belong three artefacts — mould strapping, as would be expected, a handle rivet and a patch — and two pieces of waste. A majority of bronzes fall into the 5–15% tin range, a result that makes good sense from a functional point of view; the only possible surprise is for the handle rivet (**M37**) whose tin content contrasts with its counterpart (**M36**). Two striking results are the uniformly high tin content in the three arrowheads, and the lack of leaded bronzes among the analysed assemblage; no iron was detected in any artefact. SF4 was confirmed as lead, and M170 is electrum.

Two main levels of comparison are now possible, first with the corresponding results from the neighbouring sites of Ayios Stephanos and Nichoria, and second from other sites in the Peloponnese and further afield. Bearing in mind several factors, including the different sizes of the bronze assemblages, their relative states of preservation, the proportion of the assemblage selected for analysis and according to what criteria, and the differential representation of artefact types at the three southern sites, it can be seen from FIG. H.2 that the composition ranges are broadly comparable. There are apparently more unalloyed or very low tin content artefacts at the Menelaion and Ayios Stephanos than Nichoria; the 5–11% tin range is well represented at the three sites, but only the Menelaion and Nichoria have examples of bronzes with tin contents in excess of 10%. The feature of tin in excess of 15% in the arrowheads at the Menelaion, paralleled in three of the five analysed from Nichoria,[7] raises the possibility that their function was decorative. True leaded bronzes, that is with a lead content greater than 5%, are scarce: none at the Menelaion and Ayios Stephanos, and only two at Nichoria. Arsenic is present, albeit in low concentration, in some artefacts at Ayios Stephanos and Nichoria but not at the Menelaion.

Drawing in results from further afield in the Peloponnese (TABLE H.2), the bronzes from two contrasting contexts, the Citadel House at Mycenae and Kallithea tombs, seem to be broadly similar in composition — the mode tin content being clearly in the 5–11% range — to those represented in FIG. H.2. Furthermore, there is satisfactory agreement with the corresponding picture obtained by Kayafa on prehistoric bronzes from the Peloponnese for which she had access to their compositions (obtained by variety of techniques), namely the summary pictures for MH III–LH I (109 copper/

TABLE H.2. XRF analyses by the Fitch Laboratory of Aegean prehistoric and EIA bronzes.

Material	***Site***	***Date (range)***	***No. analysed***	***Publication***
Bronzes	Menelaion	LH I–III	17	This volume
"	Ayios Stephanos	MH–LH	MH 6; LH 12; uncertain 2	Jones forthcoming
"	Nichoria	MH–EIA	MH 15; LH II–III 26; EIA 16; uncertain 6	Rapp *et al.* 1978
"	Kallithea tombs	LH III	10	To be published
"	Lefkandi	EIA	110	Jones 1980
"	Mycenae, Citadel House	LH III	28	To be published
Decorated bronze dagger	Kataraktis	LH I–II	1	Photos-Jones *et al.* 1994
Decorated bronzes	Mycenae, Prosymna, Dendra, Routsi	LH I–II	6	Demakopoulou *et al.* 1995
Copper axes	Peloponnese	FN/EB I	5	Phelps *et al.* 1979
Bronzes	Knossos, Unexplored Mansion	LM II	*c.* 140 (all artefacts except for 36 examples of scrap and 15 of waste). Results for *c.* 90 artefacts appear in Catling & Jones 1977, fig. 3	Catling and Jones 1977
"	Knossos, Sellopoulo tombs	LM IIIA	45 (incl. components of individual artefacts)	Catling and Jones 1976; and unpublished
"	Myrtos Pyrgos	LM I–II	36	To be published

[7] Rapp *et al.* 1978, table 11-4: N539 (>25% Sn), N1244 twice (11% Sn), one of them (N539) admittedly of imprecise date (MH–LH III) contrasting with 505 (3% Sn with 3% As) and arrowplate N2 (5.6% Sn).

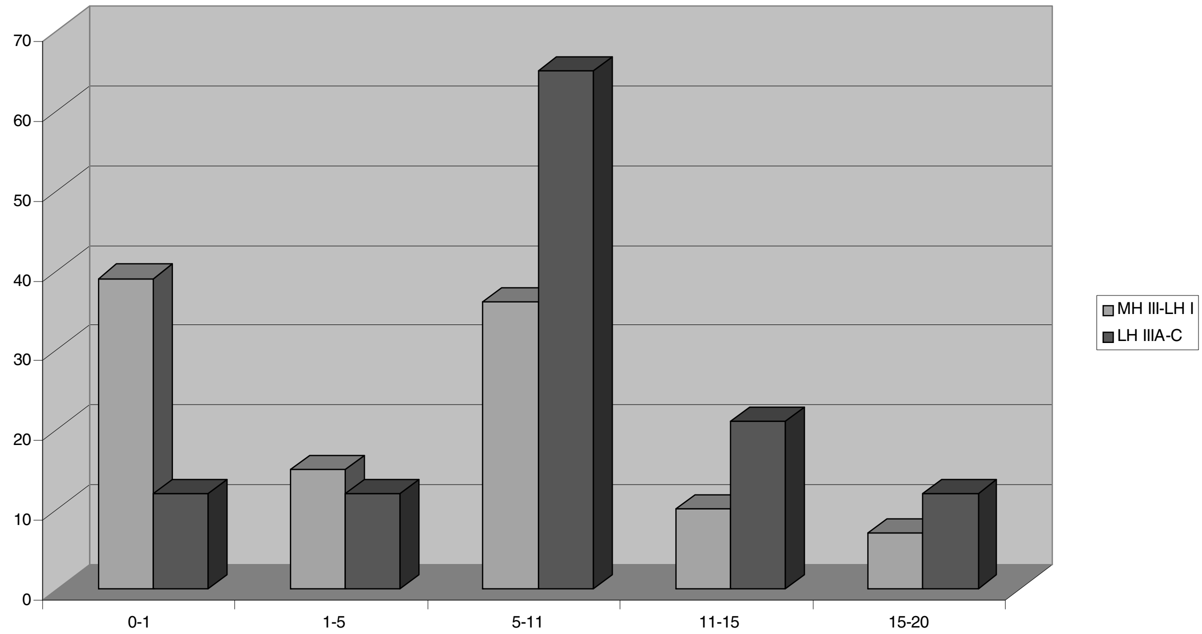

Fig. H.3. Distribution of tin contents in bronzes in the Peloponnese (from Kayafa 1999).

bronze artefacts) and LH IIIA–C (122 artefacts).[8] FIG. H.3 indicates the correspondences in the 0–1% range and the mode in the 5–11% range. As for bronzes from Late Minoan sites on Crete analysed by XRF (TABLE H.2) and AAS[9], there is one apparently striking difference with their counterparts in the Peloponnese which is the greater frequency of copper or low tin bronzes on Crete, the significant exception being the bronzes from the Sellopoulo tombs near Knossos (FIGS. H.4 *a*, *b*).

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[8] Kayafa 1999.

[9] Mangou and Ioannou 1998.

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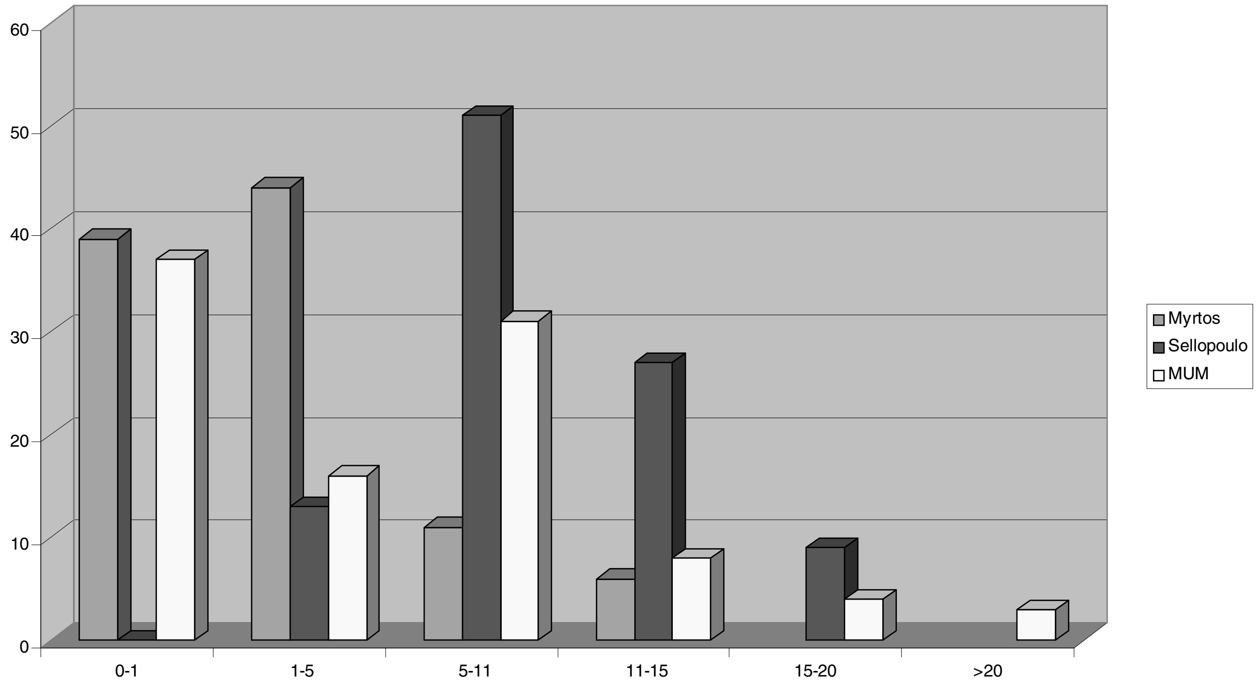
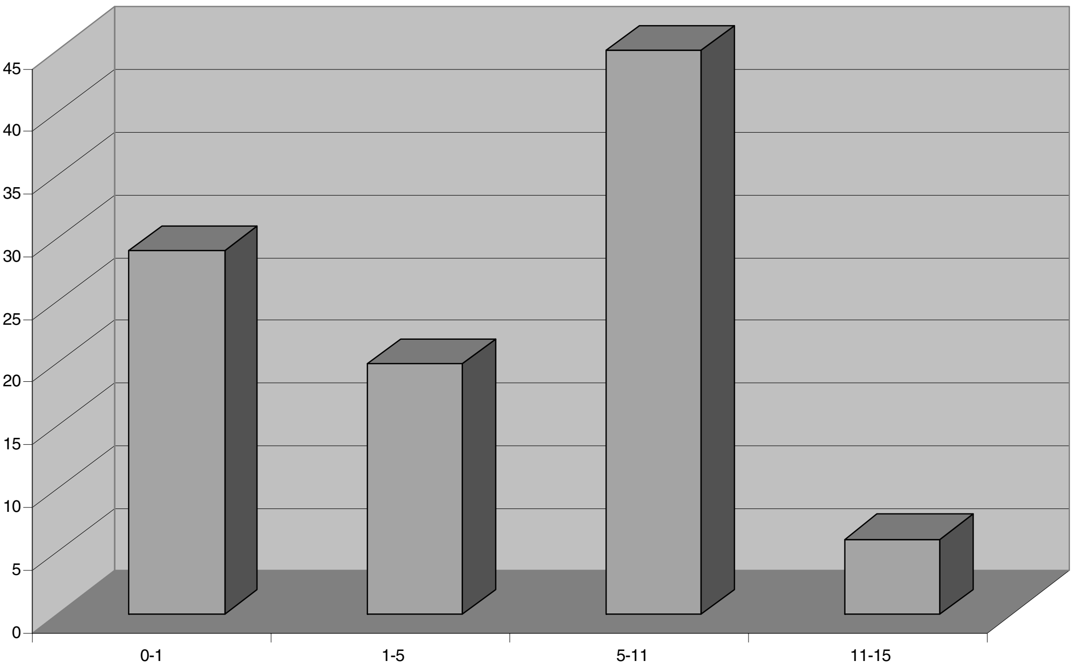


(*a*)



(*b*)

FIG. H.4. (*a*) Percentage proportions of tin ranges in LM bronzes from the Minoan Unexplored Mansion at Knossos of LM II date (Catling and Jones 1977, 90 artefacts in groups I–VIII and XI), Sellopoulo Tomb 4 of LM IIIA1 date and Myrtos Pyrgos of LM I–II date; (*b*) Percentage proportions of tin ranges in LM bronzes from Crete analysed by atomic absorption spectrometry (Mangou and Ioannou 1998).

(*a*)