

THE ISOTOPIC COMPOSITION OF TIN IN SOME ANCIENT METALS AND THE RECYCLING PROBLEM IN METAL PROVENANCING*

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A recent suggestion that some ancient metallurgical processes might give rise to large changes (> 0.5%) in the isotopic composition of tin gave hope that it might be possible to identify ancient bronze samples which had undergone recycling and mixing processes. This paper describes a method for the analysis of the isotopic composition of tin by thermal ionization mass spectrometry and applies it to analyse a number of ancient bronzes and tin metal objects from the Bronze Age Mediterranean. No observable isotopic fractionation of tin was found above $\pm 0.1\%$ in the ratio $^{122}\text{Sn}/^{116}\text{Sn}$. Consequently, either recycling of bronze in the Late Bronze Age Mediterranean was not so common as supposed, or the isotopic composition of tin is not fractionated by anthropogenic metallurgical processes to the extent predicted by the Bradford group.

KEYWORDS: MEDITERRANEAN, BRONZE AGE, MASS SPECTROMETRY, INGOT, BRONZE, TIN, ISOTOPIC COMPOSITION, ISOTOPIC FRACTIONATION, REMELTING, RECYCLING

INTRODUCTION

A recent paper (Budd *et al.* 1995a) gave a theoretical appraisal of the possible alteration of the isotopic composition of tin in some metallurgical processes. In particular it was suggested that fairly large increases in the $^{122}\text{Sn}/^{116}\text{Sn}$ ratio, up to or exceeding 0.5%, could occur in ancient bronzes subjected to remelting, and that these changes in the isotopic composition of tin could be used to detect bronze artefacts which had been subjected to remelting and recycling operations. If correct, the study of tin isotopic variations could provide a method for targeting ancient bronze artefacts for provenancing by lead isotope analysis (see, e.g., Gale and Stos-Gale 1982), for which objects which have undergone recycling are suspect, due to the danger that they may have been made from a mixture of metal from different ore sources. Here are presented the first analyses of the isotopic composition of tin in ancient metal artefacts, as a preliminary empirical evaluation of the interesting ideas of Budd *et al.* (1995a).

BACKGROUND

It is generally believed that the isotopic composition of tin in tin minerals, chiefly cassiterite, is invariant in nature. This rests on the work of De Laeter and his colleagues in Australia (Rosman, Loss and De Laeter 1984; Rosman and McNaughton 1987; McNaughton and Rosman 1991). They eventually achieved, using a double-spiking method, precisions of about 0.05% in measuring tin isotope ratios. Investigations of the isotopic composition of tin in cassiterite

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samples, chosen to include a variety of mineralogical styles and ranging from Phanerozoic to Archaean in age, and in a number of modern tin metal samples, showed no statistically significant variations of isotopic composition. It should be noted that the cassiterite samples investigated were from Australian, Nigerian, Malaysian and Cornish deposits. On the other hand, the major part of lead isotope metal provenancing studies has concentrated on the Bronze Age Mediterranean, for which quite other tin deposits are likely to have provided the tin. It may be an open question whether the isotopic composition of tin is completely invariant in all tin ore deposits, so that there may still be merit in exploring this further, since a method for provenancing the source of tin in bronzes would be of great value for Mediterranean archaeology.

Budd *et al.* (1995a) accept that tin isotopes do not appear to fractionate in natural ore forming processes or in modern, high yield, processes of smelting tin. In contrast, they aver that variations in tin isotopic composition are almost inevitable as a result of substantial losses (10–30%) of tin during the melting of tin bronzes. They attribute these losses to the evaporation of volatile tin compounds such as SnO and SnS, formed by reaction of tin metal with oxygen and/or sulphur present in the copper. They suggest that these losses of volatile tin compounds take place by non-equilibrium evaporation, by applying the thermodynamic/kinetic theory of Mulliken and Harkins (1922) (which was developed in terms of evaporation in a vacuum), they predict about a 0.5% increase in the ratio $^{122}\text{Sn}/^{116}\text{Sn}$ for the non-equilibrium evaporative loss of 20% of the tin (Budd *et al.* 1995a, fig. 1). For three successive melts of 10% tin bronze, with alloying additions of new tin at each step to maintain a constant alloy composition, an increase of about 1% in the ratio $^{122}\text{Sn}/^{116}\text{Sn}$ is predicted (Budd *et al.* 1995a, fig. 2). These changes of isotopic composition are an order of magnitude higher than the limits of natural variation in cassiterites claimed by McNaughton and Rosman (1991), and would be easily measurable. Consequently it seemed important to make some analyses of the isotopic composition of tin in samples of ancient bronzes chosen to come from the Bronze Age eastern Mediterranean *koine* for which Budd *et al.* (1995b) have hypothesized the presence of abundant recycling of bronze.

SAMPLES

Samples of Bronze Age bronze artefacts were chosen from various sites in the eastern Mediterranean forming part of the *koine* for which Budd *et al.* (1995b) have claimed that remelting and recycling was common practice. Also included are two fragmentary artefacts, which some have suggested to be part of a shipboard smith's stock in trade for remelting and incorporation into new objects, from the Bronze Age Cape Gelidonya shipwreck (Bass 1967). These objects are described in Table 1; it should be noted that the bronze toggle pins are not small, but fairly large, objects.

In developing their theories it has been assumed by Budd *et al.* (1995a) that negligible fractionation of tin isotopes occurs in smelting tin ores to produce the metal. That this is so in modern high yield tin smelting is probable, but little is known about tin smelting in the Bronze Age. If significant fractionation of tin isotopes did occur in ancient tin smelting, then, for tin in a bronze, it would become impossible to disentangle this from possible fractionation during subsequent remelting steps, which would destroy the utility of the suggestions by Budd *et al.* (1995a). Consequently we thought it advisable to make isotopic analyses for ancient tin metal objects, as well as tin bronzes. The objects analysed are described in Table 2. The Israeli tin

Table 1 Catalogue of bronze samples analysed

Sample no.	Site	Type	Sn %	Date
BWG417	Cape Gelidonya	Hoe fragment	8.1	13th C. BC
BWG-50-24A	Cape Gelidonya	Cylindrical rod	6.9	13th C. BC
L313A:72c	Lapithos (Cyprus)	Bronze pin	15.5	MC I
L316:175	Lapithos (Cyprus)	Bronze pin	16	MC II–III
KAD1	A. Dhimitrios (Cyprus)	Bronze lump	18.5	LC IIC
C475	Kalopsida (Cyprus)	Bronze pin	9.1	MC I–II

MC I \approx 1900–1800 BC; MC II \approx 1800–1725 BC; MC III \approx 1725–1650 BC; LC IIC \approx 1325–1225 BC.

ingots, apart from that from the site of Dor, came from underwater excavations off the coast of Israel; they are described by Muhly (1977), Maddin *et al.* (1977), Wachsmann and Raveh (1980), and Galili *et al.* (1986). In addition a tin sample was analysed from the seventeenth-century AD Aanloop Molengat shipwreck excavated by the Ministry of Culture of the Netherlands; this came from a tin roll bearing a heraldic stamp linking it with the Erzgebirge tin deposits. This selection of tin samples, ranging from the Bronze Age to about AD 1630 and from different geographical origins, should reflect different ore sources and ancient tin smelting practices.

ANALYTICAL METHODS

Dissolution and purification

Tin metal samples were dissolved in concentrated Romil SeastarTM ultrapure HCl, which was diluted to about 6N HCl with MilliRho/MilliQ ultra pure water. For the bronze samples it was decided to avoid the ion exchange purification method described by McNaughton and Rosman (1991), partly because it has a rather low yield of about 50%. Instead the bronze samples were dissolved in concentrated Romil SeastarTM HCl with addition of a drop of concentrated Romil SeastarTM HNO₃; tin was then precipitated as metastannic acid by addition of sufficient concentrated Romil SeastarTM HNO₃. This precipitate was then freed from copper and other

Table 2 Ancient tin metal samples and tin metal standard

Sample no.	Site	Description	Date
CMS6	Dor (Israel)	Ingot	LBA
HC1111/1	Hishuly Carmel (Israel)	Ingot	LBA
HC1111/2	Hishuly Carmel (Israel)	Ingot	LBA
81/608-5	Israel	Ingot	LBA
AM7.8.7:25	Aanloop Molengat	Tin roll	17th C. AD
STD1	(Johnson Matthey)	Puratronic 99.999%	AD 1988

LBA: Late Bronze Age.

elements by several steps of centrifugation and washing with ultrapure HNO_3 and then MilliRho/MilliQ ultrapure water. Samples, therefore, had to be isotopically analysed in the mass spectrometer either as tin metal dissolved in HCl, or as a slurry of metastannic acid; this is similar to the mass spectrometric procedures followed by Rosman *et al.* (1984).

Purity of the tin metal samples

It is important, in the mass spectrometry of tin, to avoid isobaric interferences from isotopes of Cd, Te and In (*ibid.*). Instrumental neutron activation analyses (INAA) of the tin samples used in this work were made and are reported in Table 3. The analyses show that these elements are present at very low levels in these ancient tin metal samples. The purity of the samples, together with the discrimination against thermal ionization of Cd, In and Te by the activator used (*ibid.*; Rosman and McNaughton 1987), made it unnecessary to purify them further for this study.

Mass spectrometry of tin

Mass spectrometry was carried out by thermal ionization mass spectrometry (TIMS). Tin was loaded either in 6N HCl or as a slurry of the metastannic acid with water, in both cases with an Al containing silica gel/boric acid ionization enhancement activator solution similar to that described by Rosman *et al.* (1984). The mixtures were loaded on to a single zone refined Re filament of the type described by Maeck (1992, 74–5) in his work applying a silica gel/boric acid technique to the optimum thermal ionization of Fe for high precision mass spectrometry. The optimum sandwich loading technique favoured by Maeck (1992, 76) for Fe was found also to be useful for Sn, though using the activator used for Sn by Rosman *et al.* (1984). This combination of activator, loading technique and filament design was found, for loads of 2 μg of tin metal in HCl, reliably to produce ^{120}Sn ion beams of about 0.5E^{11} A which lasted for one to two hours, at an indicated filament temperature of about 1250 $^\circ\text{C}$ as measured by an infrared pyrometer. Since plentiful amounts of tin were available for analysis, 6 μg amounts of tin metal in HCl were loaded for routine TIMS analyses though, as found also by Rosman *et al.* (1984, 284) for tin oxide samples, about an order of magnitude more sample was needed when the metastannic acid slurry was loaded.

All analyses were performed using a modified VG Isotech Isolab 54, computer controlled three-stage (E-B-E) thermal ionization mass spectrometer equipped with seven Faraday collectors and a Daly ion counting detector system. This was used in the static multi-collector mode, simultaneously collecting the masses 112, 116, 117, 118, 120, 122, 124, with an integration time of five seconds for the tin isotopes and ten seconds for background measurements. A fixed filament heating routine to operating temperature over 25 minutes was adopted

Table 3 INAA of ancient tin metal samples (concentrations in ppm)

Sample no.	Au	Ag	Cu	As	Sb	Fe	Zn	Co	Sc
CMS6	0.20	0.6	51	16	10	42	9	3	0.2
HC1111/1	2.12	0.6	5	30	7	131	10	3	0.2
HC1111/2	0.41	0.3	1	18	< 1	75	10	4	0.2
81/608-5	0.35	0.36	5	34	13	18	129	5	0.14

Cd, In, Se and Te were less than 10 ppm in all tin samples.

for all measurements; for each sample 120 ratios were taken over a time interval of 90 minutes with on average a total Sn ion beam current of $2E^{-11}$ A. The internal run precision was generally better than 0.005% on all ratios (two standard errors of the mean on 120 ratios), except for the ratio 124/112, for which the coincidence of mass 124 with mass 112 was not absolutely perfect. The modified Isolab 54 mass spectrometer was fitted with a Polycold™ 20 000 litres/second cryogenic pump directly inside the source housing; no problems were ever experienced due to emission of volatiles at running conditions (McNaughton and Rosman 1991, 501). Aliquots of all samples of tin or metastannic acid, respectively from tin metal and from the bronzes, were examined using the Daly ion counting system (background of 0.5 cps) to check for the presence of isobaric interferences from ^{115}In , checked at ^{113}In , ^{112}Cd , ^{114}Cd and ^{116}Cd , checked at ^{110}Cd and ^{111}Cd , and from ^{122}Te , ^{124}Te , checked at ^{126}Te and ^{128}Te . At ^{120}Sn ion currents of about $0.5E^{-11}$ A (about $3E^7$ ions per second), the ions per second at mass positions 110, 111, 126, 128 were uniformly below ten ions per second; consequently interferences with ^{112}Sn , ^{114}Sn , ^{116}Sn and ^{122}Sn are completely negligible. The interference from ^{115}In was not completely negligible for samples HC1111/1, HC1111/2, L313A:72C and L316:175, but in the worst case the ion beam inferred to be due to ^{115}In was 1% of that due to ^{115}Sn . In this work this problem was completely avoided by basing the investigation of possible mass fractionation on the isotopic ratio $^{122}\text{Sn}/^{116}\text{Sn}$, for which the potential interferences from ^{116}Cd and ^{122}Te had been shown, by direct measurement, to be completely negligible for all samples investigated in the present work.

RESULTS

Tin standards

Since the fractionation effects predicted by Budd *et al.* (1995a), and investigated here, are large compared even with the reproducibility of tin isotope ratio data reported by Rosman *et al.* (1994) using a single collector mass spectrometer, it was decided in these preliminary investigations not to use a double-spike (as did Rosman and McNaughton 1987). In order to determine the reproducibility of tin isotope ratio analyses using our VG Isolab 54 instrument an internal laboratory tin standard was used, consisting of Johnson Matthey Puratronic Grade 1 tin metal (Batch W14222), dissolved and held in solution in 6N HCl at a concentration of 5000 μg Sn per ml of solution. Work reported by Rosman *et al.* (1984) suggested that the correction factor per AMU for fractionation effects in the mass spectrometer differed according as to whether tin was loaded on to the filament as oxide or electroplated as the metal on to the filament. Consequently one series of isotopic analyses of the Puratronic standard was made by loading a number of filament beads with 6 μg aliquots of the chloride stock solution. In another series of isotope ratio analyses metastannic acid was precipitated from the chloride Puratronic stock standard solution, using concentrated HNO_3 , and tin was loaded as an aqueous slurry of the metastannic acid.

Table 4 presents the overall means and 95% errors for the tin isotope ratios measured for ten separate filament beads loaded directly from the chloride solution. These are not the raw data, but have been obtained by comparing the raw ratios measured in Oxford for $^{112}\text{Sn}/^{120}\text{Sn}$, $^{117}\text{Sn}/^{120}\text{Sn}$, $^{118}\text{Sn}/^{120}\text{Sn}$, $^{122}\text{Sn}/^{120}\text{Sn}$ and $^{124}\text{Sn}/^{120}\text{Sn}$ with those published by Rosman *et al.* (1984, 287) for their MS β mass spectrometer. For each comparison a fractionation constant F per

Table 4 Mean data for ten separate loads of the Puratronic standard as chloride (the errors are the bounds of the 95% confidence interval computed using Student's *t* distribution)

$^{124}\text{Sn}/^{120}\text{Sn}$	$^{122}\text{Sn}/^{120}\text{Sn}$	$^{118}\text{Sn}/^{120}\text{Sn}$	$^{117}\text{Sn}/^{120}\text{Sn}$	$^{116}\text{Sn}/^{120}\text{Sn}$	$^{122}\text{Sn}/^{116}\text{Sn}$
0.177563	0.142135	0.74302	0.23542	0.44606	0.318596
± 0.000084	± 0.000053	± 0.00020	± 0.00009	± 0.00035	± 0.000089

atomic mass unit was calculated, assuming a linear fractionation law, according to formulae analogous to:

$$R_{\text{true}}(120/116) = (1 + 4F) \cdot R_{\text{observed}}(120/116) \quad (1)$$

The mean *F* value was then calculated from all these comparisons as 0.002136 ± 0.000069 (one standard deviation). This *F* value was then applied, according to formulae analogous to that quoted above, to the raw Oxford data, arriving at the data reproduced in Table 4.

A comparison of our data with those presented by Rosman *et al.* (*ibid.*) shows good agreement; all ratios agree within 0.02%. Note that comparison could not be made to the more precise data for a tin standard, obtained using a double-spike and a multi-collector ion collection system, reported by Rosman and McNaughton (1987). When attempts were made to do this, inconsistent *F* values were obtained from the comparison of different ratios; note, for comparison with the values given above, that in their 1987 paper Rosman and McNaughton record data which, for example, yield the ratios $^{116}\text{Sn}/^{120}\text{Sn} = 0.450999$ and $^{122}\text{Sn}/^{116}\text{Sn} = 0.313355$, and normalize all their data to $^{118}\text{Sn}/^{120}\text{Sn} = 0.747$, in contrast to the value of 0.74295 quoted by Rosman *et al.* (1984) (in which they normalize to $^{116}\text{Sn}/^{120}\text{Sn} = 0.446$). These factors make, of course, no difference to the conclusions drawn in the 1987 or 1991 Australian papers (Rosman and McNaughton 1987; McNaughton and Rosman 1991), since the double-spike and normalization procedures were applied to standards and samples in the same way in these papers.

Figure 1 (a) plots the Oxford data obtained for the Puratronic standard, corrected as outlined above, for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$. In what follows this ratio is used throughout, since it has the largest mass difference of the ratios measured reliably in this work and is therefore most sensitive to fractionation effects potentially induced by metallurgical processes; moreover it is the ratio which figures in the predictions made by Budd *et al.* (1995a, figs. 1 and 2). A plot of the individual data for this ratio, whose mean and 95% confidence limits are given in Table 4, appears in Figure 1 (a). Though the 95% confidence limits for these data are $\pm 0.028\%$ of the mean ratio, the range in the data is $\pm 0.065\%$ of the mean; this is perhaps better reflected in a graph of the data for the standard, to which individual $^{122}\text{Sn}/^{116}\text{Sn}$ measurements for ancient tin samples can be compared visually. A last feature of the data for the Puratronic tin standard, run as the chloride, is brought out by taking the raw data and, in place of comparing the raw data ratio by ratio with that of Rosman *et al.* (1984) to calculate a mean *F* value, to normalize the raw ratios by adjusting to a value of $^{116}\text{Sn}/^{120}\text{Sn} = 0.4460$ (Devillers *et al.* 1983), using linear relations of the type of equation (1). The data so normalized for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$ are plotted in Figure 1 (b); this normalization results in a reduction in the 95% confidence error to about $\pm 0.017\%$, with a mean ratio within 0.04% of the value measured by Rosman *et al.* (1984). Note that in both Figures 1 (a) and (b) the data plotted from Rosman *et al.* (1984) are normalized to

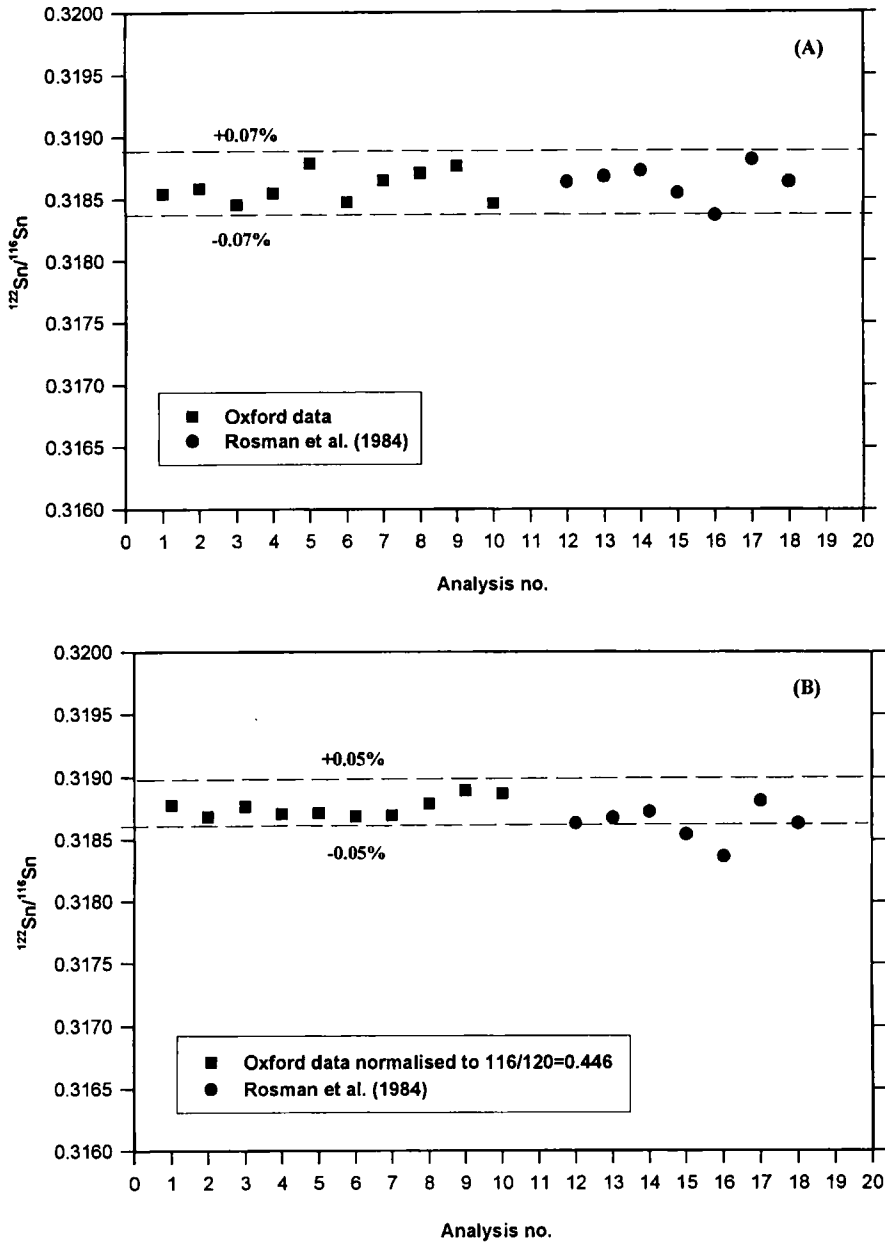


Figure 1 (a) Isotopic analyses of the Puratronic internal laboratory tin standard run as the chloride, compared with data reported by Rosman et al. (1984) for their internal standard. The Oxford data were corrected in terms of Rosman et al. (1984) (see the text). The mean of the Oxford data = 0.318596, with a 95% confidence error of 0.000089. (b) Oxford data for the Puratronic internal tin standard run as the chloride: the raw data have been normalized to $^{116}\text{Sn}/^{120}\text{Sn} = 0.446$; these data are compared with those of Rosman et al. (1984), which were normalized in the same way. The mean of the Oxford data = 0.318758, with a 95% confidence error of 0.000054.

Table 5 Mean data for ten separate loads of the Puratronic standard as metastannic acid (the errors are the bounds of the 95% confidence interval computed using Student's *t* distribution)

$^{124}\text{Sn}/^{120}\text{Sn}$	$^{122}\text{Sn}/^{120}\text{Sn}$	$^{118}\text{Sn}/^{120}\text{Sn}$	$^{117}\text{Sn}/^{120}\text{Sn}$	$^{116}\text{Sn}/^{120}\text{Sn}$	$^{122}\text{Sn}/^{116}\text{Sn}$
0.177610	0.142150	0.74297	0.23539	0.44628	0.31851
± 0.000059	± 0.000025	± 0.00011	± 0.00008	± 0.00046	± 0.00015

$^{116}\text{Sn}/^{120}\text{Sn} = 0.4460$, since the raw data are not given in their paper. This normalization, in terms of a fixed internal ratio for $^{116}\text{Sn}/^{120}\text{Sn}$, is closely similar to the use of a double-spike to remove fractionation effects in the mass spectrometer. However, since the potential fractionation effects which we are investigating, due to metallurgical processes, are also likely to be dependent on mass difference, we cannot use this approach in terms of adjusting to a constant $^{116}\text{Sn}/^{120}\text{Sn}$, since such a normalization is very likely to normalize out any real fractionation effects which may be present.

A separate sequence of data was run for the Puratronic tin standard loaded as metastannic acid; the data, normalized as before to the data reported by Rosman *et al.* (1984), are summarized in Table 5. The mean *F* value for these data was found to be 0.002644 ± 0.000112 (one standard deviation), which is clearly higher than the *F* value quoted above for Sn loaded as the chloride, but not by so large a factor as found by Rosman *et al.* (1984) between running Sn as the oxide or the electro-deposited metal. The ratios reported in Table 5 for analyses made by loading Sn as metastannic acid agree within 0.05% of those reported by Rosman *et al.* (1984) for their MS β mass spectrometer. A plot of the individual data for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$ appears in Figure 2. Though the 95% confidence limits for these data are $\pm 0.048\%$ of the mean ratio, the range in the data is $\pm 0.087\%$ of the mean. As for the analyses made using the chloride, this is perhaps better reflected in a graph of the data for the standard run as metastannic acid, to which individual $^{122}\text{Sn}/^{116}\text{Sn}$ measurements for ancient tin samples can be compared visually.

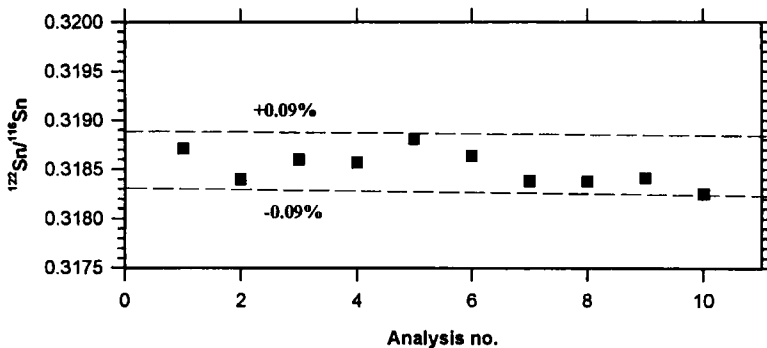


Figure 2 Oxford data for the Puratronic tin standard run as metastannic acid and normalized via *F* constants (see the text) to the data reported by Rosman *et al.* (1984). The mean of the Oxford data = 0.31851, with a 95% confidence error of 0.00015.

Ancient tin metal samples

The samples of ancient tin described above were dissolved in HCl and analysed directly as the chloride. The data obtained for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$, normalized using the average F value obtained from the Puratronic standard run as the chloride, are plotted in Figure 3 in comparison with the data for the standard. To increase confidence in the data for the tin metal samples, two independent isotopic analyses were made for each sample, which in all cases are in good agreement with each other. It is clear that there is no evidence from this work of fractionation of tin isotopes in the ancient tin smelting processes which were responsible for the production of these ancient tin objects; if there is a fractionation effect it is less than 0.1%. The Australian work (McNaughton and Rosman 1991) had of course already established, for five samples of modern tin, that there was no measurable fractionation of the isotopic composition of tin. This was not altogether unexpected, given that isotope fractionation is not present in the tin ores from which they were smelted since, as mentioned by Budd *et al.* (1995a, 128), modern tin smelting recovers tin with high yields. However, this was not so in the past. Apart from considerable loss of tin to the slag (in processes which are not expected to fractionate isotopes), there were also large losses to furnace fumes; as Gowland (1930, 519) wrote 'The greatest difficulty of the tin smelter in the past has been the loss of tin by volatilisation during smelting operations'. Such large losses were indeed recorded by Gowland (1899, 294–5) even for tin smelting as practised as late as AD 1883 at Taniyama in Japan. If losses of tin through the evaporation of volatile tin compounds during bronze melting can, *pace* the suggestions of Budd *et al.* (1995a), cause relatively large changes of the isotopic composition of tin, it is not clear to the author why this might not occur in volatile losses during inefficient ancient tin smelting, but it clearly has not occurred to any great extent, if at all, for the samples of ancient tin metal investigated here. However, if the samples analysed here are sufficiently representative of anciently produced tin metal, then it would seem that ancient tin smelting does not produce significant pre-existing tin isotope anomalies in the tin metal originally used to make ancient bronze alloys which, if they had existed, would have masked the predicated isotopic fractionation due to disequilibrium evaporation of tin during remelting of bronzes.

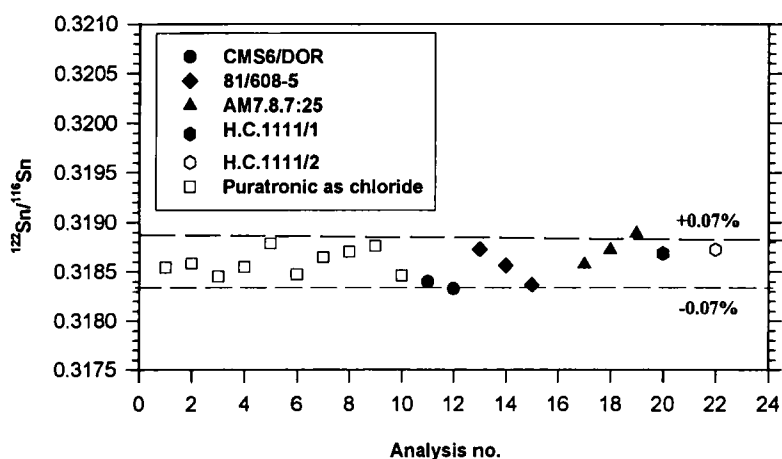


Figure 3 Isotopic composition of tin in ancient tin metal samples compared with the Puratronic tin standard. All samples were loaded as the chloride.

Ancient tin bronzes

The samples of ancient bronzes described above were dissolved in HCl, metastannic acid precipitated using HNO_3 , and purified by successive centrifugation and washing steps as described above, and analysed directly as metastannic acid. The data obtained for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$, normalized using the average F value obtained from the Puratronic standard run as metastannic acid, are plotted in Figure 4 in comparison with the data for the standard; two independent isotopic analyses were made for each bronze. It is clear that there is again no evidence from this work of fractionation of tin isotopes in the six bronzes analysed, or at least no effect beyond about 0.1%. There certainly are no changes in this ratio of the order of 0.5% or more, as suggested by Budd *et al.* (1995a, figs. 1 and 2); these authors predict that this ratio would increase to about 0.320 after only one melting.

It should perhaps be mentioned that, though the visual comparisons of the data in Figures 2 and 3 here are probably sufficient to show that there is no evidence for isotopic anomalies in the tin of either the metallic tin samples or the tin bronzes, this was confirmed also by statistical tests of the data for the samples in comparison with the data for the standards, using both unpaired t-tests and Mann-Whitney rank sum tests.

CONCLUSIONS

This study has shown that the isotopic composition of tin can be measured with sufficient accuracy to look for the large changes predicted by Budd *et al.* (1995a) as occurring in remelted ancient bronzes without the use of a double-spike, by using a modern computer-controlled multi-collector thermal ionization mass spectrometer fitted with an ion counting Daly detector for investigating possible isobaric interferences. Satisfactory isotopic analyses can be made using tin in either chloride or metastannic acid form, though the former requires far less sample to be loaded. For both the ancient tin metal and bronze samples analysed, the fractionation of tin isotopes either did not exist or is below 0.1% for the ratio $^{122}\text{Sn}/^{116}\text{Sn}$. The absence of isotopic fractionation in the tin samples extracted from the ancient bronzes could be due either to

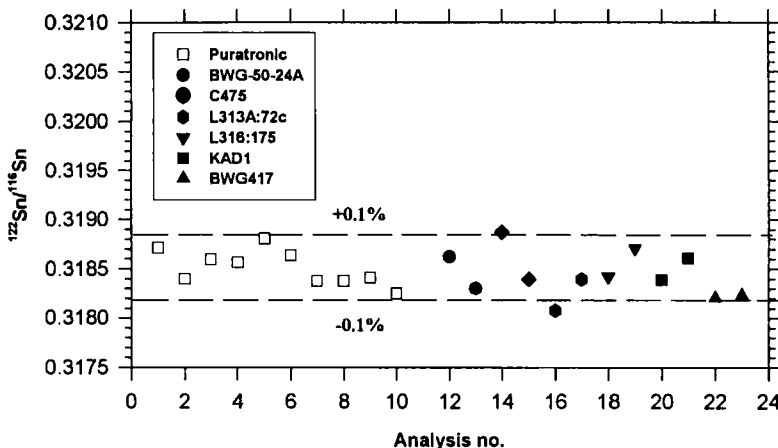


Figure 4 Isotopic composition of tin extracted from ancient bronzes and loaded as metastannic acid, compared with data for the Puratronic standard, also loaded as metastannic acid.

the non-existence of the mechanisms and models proposed by Budd *et al.* (1995a), or alternatively that these particular samples never experienced remelting after the tin bronze alloys were initially made.

The bronzes analysed here were selected for investigation on the grounds that they came from within the *koine* of metal production and distribution for which Budd *et al.* (1995b) have suggested widespread mixing together of metals; indeed two came from the very Cape Gelidonya ship, containing 'an itinerant bronzesmith's stock-in-trade' (Knapp and Cherry 1994, 143), which had clearly been tramping copper and bronze about the Mediterranean for barter. Others come from Cyprus, where the closely similar isotopic compositions of lead in the oxide ingots was suggested by Budd *et al.* (1995b) to have been the result of widespread mixing of metals from different sources. The sample is admittedly small in size but, if Budd *et al.* (1995b) are right about the widespread mixing of metals in this *koine* (for which there is remarkably little real archaeological evidence), it would be surprising if our selection of objects included no example of a remelted and mixed metal.

However, it does seem to the author that Budd *et al.* (1995a) may have neglected several points in constructing their models and arguments, one of which is the question why, if disequilibrium evaporation of volatile phases such as SnO and SnS could occur during remelting, could it not have occurred also in the initial manufacture of a tin bronze alloy in antiquity? The copper metal used to make such an alloy would have contained dissolved oxygen and most likely also some sulphur, so that loss of volatile compounds of tin seems as likely at the very first melting/alloying step as at a subsequent remelting step (indeed Budd *et al.* 1995a, 129, mention that experiments at Bradford 'showed that 10–30% of the tin alloying addition evaporated during the *alloying* and casting of a series of Cu-Sn-Sb alloys' [my italics]). If the tin isotopic fractionation effects postulated by Budd *et al.* (1995a) occur on remelting an alloy, there seem to be no reasons why they should not occur also at the time of the original manufacture of the bronze alloy. In fairness Budd *et al.* (1995a, 129) do seem to recognize this, but do not seem to draw the conclusion which I now present.

This seems to have the implication, fatal to Budd *et al.*'s hypotheses, that a tin isotopic anomaly found in an ancient tin bronze would not allow one to draw the conclusion that this bronze had necessarily undergone remelting (and possible mixing), since the anomaly might have resulted when the bronze alloy was made for the first time by adding tin to molten copper. The implication for the present study may be that, since no (or very small) tin isotopic anomalies have been found, tin isotopes are not appreciably fractionated by even fairly high losses of tin as volatiles during alloying, and tin isotopic anomalies greater than about 0.1% are consequently not likely to occur due to tin losses during remelting. The next step might be thought to be the study of tin isotope compositions in a suite of tin bronzes, containing dissolved oxygen and some sulphur, which had deliberately been remelted many times to cause substantial losses of tin; parallel experiments on tin isotopic compositions associated with losses of tin during alloying should be made. Certainly if such extreme experiments revealed minimal changes in the isotopic composition of the tin, then the suggestions of Budd *et al.* (1995a) would be laid to rest. If, however, tin isotopic anomalies were found, the question how nearly the experiments approximated ancient processes would have to be considered, and a much more extensive survey of the sort begun here on ancient bronzes carried out, using the double-spike method to ensure that even anomalies much smaller than those predicted by Budd *et al.* (1995a) could be detected. At the same time it should not yet be assumed that cassiterites from ore deposits likely to have supplied the Mycenaean, Cypriot and Minoan worlds display no small tin isotope anomalies.

Finally, this study does seem to have shown that isotopic fractionation changes in the isotopic composition of tin greater than 0.1% are not commonly present in ancient tin metal or ancient bronze alloys. This may imply either that remelting of bronze was not common in the Late Bronze Age Mediterranean, or that the theoretical processes which Budd *et al.* (1995a) postulate are not valid for ancient remelting processes.

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NOTE ADDED IN PROOF

F. Begemann (Mainz) pers. comm. 7 October 1996 regarding his high precision, double-spiked, Sn isotope analyses: for a heated bronze which had lost 10% Sn his data yield a change in $^{122}\text{Sn}/^{166}\text{Sn}$ of c. 0.048%, well below the 0.235% predicted by Budd *et al.* (1995a).