



Copper ingots from a probable Bronze Age shipwreck off the coast of Salcombe, Devon: Composition and microstructure



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ABSTRACT

The seabed site of a probable Bronze Age shipwreck off the coast of Salcombe in south-west England was explored between 1977 and 1982 and from 2004 onwards. Nearly 400 objects including copper and tin ingots, bronze artefacts/fragments and gold ornaments were found, typologically dating either to c. 1300–1150 BC or 1000–800 BC. The 280 copper and 40 tin plano-convex ingots and ingot fragments represent the largest discovery, measured by total weight as well as by quantity, of plano-convex or bun ingots in northwest Europe. The Salcombe copper ingots provided a wonderful opportunity for the technical study of copper ingots in a probable shipwreck context, as opposed to terrestrial contexts of deliberate deposition. The chemical composition of 25 plano-convex copper ingots was determined using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Two artefacts from the site were also analysed for comparison with the ingots. Following the compositional analysis, a microstructural study was carried out on ten Salcombe copper ingots selected to cover those with different sizes, shapes and variable impurity levels using metallography and scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS).

All the analysed copper ingots are of unalloyed copper with low levels of impurities. Sulphide inclusions are present in all samples and bulk sulphur contents are of 0.32–0.79% in the ingots but lower in the artefacts. The Salcombe ingots were found to have a quite similar impurity pattern to the Hertford Heath (England) ingots (except for iron content). They are distinctly different from the Uluburun ingots, and, to a lesser degree, from Sardinian ingots. The results are inconclusive as to how the Salcombe ingots were made. On the one hand, the very low concentration of iron and the absence of cuprite inclusions suggest that the ingots were primary smelting products of the primitive smelting process rather than produced from re-melting or refining of primary smelting lumps. On the other hand, the dense metal with very low porosity suggests the product of refining and re-casting operations under reducing conditions. However, the small ingots are not likely to have resulted from breaking of large ingots. The chemical compositions of the Salcombe ingots point to British or Western European sources although the connection with other regions cannot be excluded for some of the ingots. Further studies including lead isotope analysis are needed to address the question of provenance of the copper ingots, which would contribute to the re-emerging debates surrounding the European Bronze Age metal trade.

1. Introduction

The extraction and movement of copper throughout northwest Europe and beyond during the Bronze Age (c. 2200–800 BC) have been investigated and discussed extensively for over a century (Evans, 1881; O'Brien, 2015). The 'metals trade' – whether in copper, tin, bronze or gold – in northwest Europe continues to play a key role in societal narratives and discussions of social change, especially within the

context of the Atlantic (Radivojević et al., 2018). The extensive sources of copper ore found throughout parts of Ireland, the Isle of Man and west Britain were exploited from at least c. 2400 BC (O'Brien, 2015; Timberlake, 2017). The earliest evidence comes from the Ross Island mine, southwest Ireland (O'Brien, 2004). Surveys and excavations have established extensive radiocarbon-dated evidence for Early Bronze Age (c. 2200–1600 BC) copper mining in southwest Ireland as at Mount Gabriel (O'Brien, 1994), central and north Wales as at Copa Hill,

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Cwmystwyth (Timberlake, 2003) and the Great Orme (Dutton and Fasham, 1994; Williams, 2014), and northwest and central England as at Alderley Edge (Timberlake and Prag, 2005) and Ecton Hill (Timberlake, 2014). In southwest England, there is only one radiocarbon-dated possible copper mine, at Roman Lode, Exmoor, Devon, which yielded dates of c. 1950–1750 BC (Juleff and Bray, 2007). The copper sources in northwest France and Scotland could well have been exploited during this period, but there are currently no radiocarbon-dated sites. The next closest copper ore sources are found in northern Spain, southern France and the western Alps, hundreds of kilometres away, and were mined throughout the Bronze Age (Huelga-Suarez et al., 2012; Huelga-Suarez et al., 2014a,b; O'Brien, 2015).

The current evidence in northwest Europe indicates that only two copper mines – the Great Orme in northwest Wales (Williams, 2014; Smith et al., 2015) and Derrycarhoon in southwest Ireland (O'Brien and Hogan, 2012) – were exploited beyond c. 1600–1500 BC. Explanations for this apparent cessation of copper extraction across northwest Europe have tended to emphasise a transition towards the importing of bronze from the continent and the recycling of existing bronze objects (Rohl and Needham, 1998; Timberlake, 2017). Williams (2017) has proposed that in Britain, the mostly small copper mines with low grade ore, and lacking substantial secondary ores were superseded from c. 1600 BC–1400 BC by the large, very rich and easily worked Great Orme mine. However, the lead isotope and trace element data indicate that the Great Orme mine played only a limited role in copper production and consumption in Britain after c. 1400 BC. What is not currently determined, either archaeologically or archaeometallurgically, is where Bronze Age communities in Britain obtained their copper (or indeed tin) from c. 1400 BC onwards. The existence of spatially and chronologically distinctive metal compositions in bronze metalwork assemblages spanning c. 1400–800 BC (Northover, 1982a; Williams, 2017) demonstrates that any explanation must involve the exploitation of new copper ore sources and cannot rely solely on recycling (cf. Radivojević et al., 2018). The destruction of Bronze Age mines by later mining activity, especially for copper and tin mining in southwest England (Craddock and Craddock, 1996), should not be ignored. The existence of only one radiocarbon-dated and archaeometallurgically studied copper smelting site from the entire Bronze Age in Britain, at Pentwyn, near the Great Orme copper mine, north Wales, which dates to c. 1000–800 BC or the Late Bronze Age (Smith et al., 2015), would appear to support the large-scale importation of copper and/or bronze. Whilst the potentially archaeologically ephemeral nature of Bronze Age copper smelting should not be ignored (Timberlake, 2007; Williams, 2014), this current absence of primary production evidence stands in contrast to the now-extensive evidence for the secondary melting and (re-) casting of bronze, especially during the Middle-Late Bronze Age (c. 1600–800 BC) throughout southern England (Needham, 1980; Medlycott and Brown, 2013; Knight, 2014; Jones et al., 2015; Webley and Adams, 2016; Adams et al., 2017). There is also a vast quantity and range of Middle-Late Bronze Age bronze objects being deliberately deposited, with the highest concentrations in southern and eastern England, frequently far from any copper ore sources (Yates and Bradley, 2010; Roberts et al., 2013; Brandherm and Moskal-del Hoyo, 2014; Knight et al., 2015). Finally, the findspot distribution patterns of Middle-Late Bronze Age metal object types across southern England – whether weapons, tools or ornaments – are frequently also found in northern France, Belgium and beyond (O'Connor, 1980; Needham et al., 2013). Yet the debates on presence or absence of primary copper, tin and thereby tin-bronze production and subsequent trade in Middle-Late Bronze Age Britain are far from being over.

The discovery of 40 plano-convex or bun-shaped tin ingots weighing 18.45 kg in total, typologically dated by association either to c. 1300–1150 BC or 1000–800 BC or the late Middle-Late Bronze Age, off the coast of Salcombe has provided the most extensive, direct evidence for Bronze Age tin production and trade in Europe (Wang et al., 2016a). In addition to the tin ingots, the Salcombe seabed assemblage yielded

280 copper or copper alloy plano-convex ingots and ingot fragments, making it the largest discovery, measured by total weight (62.43 kg) as well as by quantity, of Bronze Age (c. 2200–800 BC) copper or copper alloy plano-convex ingots in northwest Europe.

The Salcombe site actually comprises two named sites 400 m apart within an open bay at the mouth of an estuary – Moor Sand and Salcombe B – where two groups of Bronze Age objects have been found between 50 and 400 m off the coastline (Fig. 1). Archaeological work at Moor Sand occurred between 1977 and 1982, led by Philip Baker and Keith Muckelroy (Muckelroy, 1980, 1981) whilst work on Salcombe site B started later in 2004 by the South West Maritime Archaeology Group (www.swmag.org) and remains ongoing (see Needham et al., 2013, 3–15 for the research history at the site). These excavations (spanning the years 1977–1982 and 2004) at the Salcombe site (Moor Sand and Salcombe site B) have been recently published with extensive environmental, archaeometallurgical and archaeological analyses (Needham et al., 2013). The investigations together recovered 31 objects including bronze objects of 22 weapons/fragments, one palstave-adze, one cauldron handle, one rectangular block/weight, one Sicilian *strumento con immanicatura a cannone*, three gold objects/fragments, an iron awl with a bone handle and a tin lump (Needham et al., 2013). In the absence of surviving organic material suitable for radiocarbon dating, detailed typo-chronological analyses of diagnostic bronze and gold objects, supported by radiocarbon dates from terrestrial sites containing comparable metalwork, placed the Salcombe assemblage in the Middle Bronze Age Penard metalwork phase (c. 1300–1150 BC) with the exception of one Type Nantes bronze sword which typologically dated to the Late Bronze Age Ewart Park metalwork phase (c. 1000–800 BC) (Needham and Giardino, 2008; Needham et al., 2013; Brandherm and Moskal-del Hoyo, 2014). Compositions of the bronzes as well as the high purity of the tin lump are consistent with this dating (Northover, 2013). The analysis of the sea level history and coastal geomorphology demonstrates that coastal retreat cannot explain the distribution of the metalwork and it is therefore argued that the objects were transported to their location before being dispersed on the seabed (Needham et al., 2013). The prevalence of later shipwrecks – Salcombe B was only found in the course of the investigation of a 17th century AD shipwreck site termed Salcombe A – suggests an accidental shipwreck or deliberate/votive shipwreck with objects eventually dispersed across the Moor Sand and Salcombe B sites. However, the presence of Bronze Age metalwork that is conventionally dated two centuries apart also implies two distinct events (Needham et al., 2013).

Further investigations at the Salcombe B site from 2005 to 2013 yielded finds that include 280 copper or copper alloy and 40 tin plano-convex ingots, 15 bronze objects and nine gold ornaments. The tin ingots have been recently published (Wang et al., 2016a), the copper/copper alloy ingots are the subject of this paper, and the gold ornaments and the bronze tools and weapons will be studied in subsequent papers. All finds have been acquired by the British Museum, are registered and have been catalogued on Collections Online (http://www.britishmuseum.org/research/collection_online/search.aspx?searchText=Salcombe).

Due to their morphological simplicity, neither the copper/copper alloy nor the tin ingots are especially typo-chronologically diagnostic (Gomez-Ramos, 1993; Bachmann et al., 2002/3; Le Carlier et al., 2014; Wang et al., 2016a). The bronze rapiers and palstaves as well as the gold twisted torc fragments and twisted wire bracelets all indicate a Middle Bronze Age Penard phase date (c. 1300–1150 BC) (see Collections online). However, the Ewart Park type bronze sword can only be placed in the Late Bronze Age Ewart Park phase (c. 1000–800 BC) and is therefore contemporary with the previously discussed earlier find of the Type Nantes bronze sword from the site. The absence of any terrestrial bronze or copper ingots in Britain during the earlier date range (Needham, 2017), as opposed to their relative ubiquity in the later date range – see (Pearce, 1983; Knight et al., 2015) for a comprehensive Bronze Age metalwork catalogue for southwest England – is not



Fig. 1. Bronze Age copper ingots in Britain. See Table 3 for analytical technique in determining composition and references.

1. Heathery Burn, Co. Durham 2. Gilmonby, Co. Durham 3. Beeston Regis, Norfolk 4. Stuntney, Cambridgeshire 5. Reach Fen, Cambridgeshire 6. Rook Hall, Essex 7. Wickham Bishops II, Essex 8. Hertford Heath, Hertfordshire 9. Hanningfield, Essex 10. Watford, Hertfordshire 11. Vange, Essex 12. Mucking, Essex 13. Stoke Hoo, Essex 14. Boughton Malherbe, Kent 15. Cliff End, Kent 16. Wickham Park, London 17. City (St Thomas), London 18. Fairfield St, London 19. Thames Bank, London 20. Runnymede, Surrey 21. Petters Sports Field, Egham, Surrey 22. Weston Wood, Surrey 23. Stogursey, Somerset 24. Gitisham, Devon 25. Mountbatten, Devon 26. Freshwater West, Pembrokeshire 27. Porthcothan, Cornwall 28. Truro College, Cornwall 29. Gillan, Cornwall 30. St Erth I and II, Cornwall 31. St Michael's Mount, Cornwall.

sufficient grounds to propose a finer temporal resolution for the copper ingots due to the maritime context of the find. Hence, whilst the copper ingots have an overall date range of c. 1300–800 BC, they could either be c. 1300–1150 BC or c. 1000–800 BC based upon the typo-chronology of the two groups of potentially associated bronze and gold metal objects.

Bronze Age plano-convex or bun ingots have been reported from numerous sites in Britain, Ireland and Western Europe and compositional analyses have been reported for some of these finds. Most of the Late Bronze Age copper ingots in Britain were analysed by Peter Northover (1980, 1982a,b, 1988a,b, 1991, 2014; in Brown et al., unpublished) using electron probe microanalysis (EPMA). Recent

compositional analysis by Armada et al. (pers. comm.) of metalwork which included ingots from the Boughton Malherbe hoard (Kent) (Adams, 2017), one of the largest Late Bronze Age hoards in Britain, was mainly by portable X-ray fluorescence spectroscopy (pXRF) with some being analysed by ICP-MS. Since all these ingots (with a few exceptions) are unalloyed copper, compositional data for them obtained by EPMA or pXRF do not provide enough chemical information needed to study the Bronze Age trade. Determination of trace elements requires analytical techniques with higher accuracies and lower detection limits, e.g. atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS) or neutron activation analysis (NAA). Compositional analysis of British Bronze Age copper ingots by these techniques is rare and has only been carried out on a few sites, e.g. Hertford Heath (Craddock and Tite, 1979), Runnymede Bridge (Hook, 1988; Rohl and Needham, 1998), Beeston Regis hoard (Lawson, 2014); and St. Michael's Mount (Young, 2015). In addition, two large groups of Bronze Age bun ingots in the Mediterranean region – one from Sardinia (Maddin and Merkel, 1990; Begemann et al., 2001) and the other from the shipwreck of Uluburun (Hauptmann et al., 2002) – were chemically analysed using these techniques.

The Salcombe copper ingots provide a relatively rare opportunity to analyse directly the Bronze Age 'copper trade'. The copper ingots vary in size and weight as well as in shape although they are generally bun-shaped (Table 1, Fig. 2). The surface of these ingots is smooth although covered with red and green corrosion products.

In this paper the compositional analysis of the Salcombe copper ingots was carried out using ICP-AES and ICP-MS, allowing many questions to be investigated, such as whether the ingots are unalloyed copper or copper alloys, whether there is any significant variation in their composition and whether their composition resembles that of any other group of ingots. Due to time and budget limits only 25 of these ingots (listed in Table 1) were selected for this pilot study to cover a variety of sizes, weights and shapes. Two artefacts, a rapier (2010,8032.17) and a palstave (2010,8032.23), were also analysed for comparison with the artefacts previously analysed by Northover (2013) and with the ingots.



Fig. 2. Copper ingots from the Salcombe site.

Following the compositional analysis, metallurgical samples were taken from 10 Salcombe ingots to cover those with different sizes, shapes and variable impurity levels. This was carried out to investigate the composition and distribution of impurity inclusions in the copper matrix. Among published trace element analyses by bulk quantitative techniques (AAS, NAA, ICP-AES and ICP-MS), only three groups - two from the Mediterranean region: the shipwreck of Uluburun (Hauptmann et al., 2002) and Sardinia (Maddin and Merkel, 1990; Begemann et al., 2001), and one from Hertford Heath (Craddock and Tite, 1979), England are large enough in sample size and, therefore, suitable for comparison with the Salcombe ingots. We will discuss whether the compositions connect the Salcombe ingots to any analysed bun ingots found elsewhere. It will also place the copper ingots from Salcombe within the context of current evidence relating to Bronze Age copper production, movement and ingot deposition in northwest Europe.

Table 1

Weight and dimensions of the copper ingots studied.

Reg. No (2010,8032.*)	Relative size	Complete/fragment	weight (g)	length (mm)	width (mm)	thickness (mm)
100	Large	Fragment	614	85	58	23
101	Large	Fragment	810	104	71	26
103	Large	Complete	958	105	82	25
181	Large	Complete	378	79	48	25
183	Large	Fragment	446	77	59	26
184	Medium	Fragment	100	42	30	16
190	Large	Complete	1524	124	110	32
196	Large	Fragment	579	95	63	22
201	Large	Fragment	900	122	83	24
202	Large	Fragment	557	74	71	28
203	Large	Fragment	941	98	79	28
220	Medium	Fragment	236	59	41	28
226	Medium	Fragment	283	65	26	21
232	Large	Fragment	529	75	46	33
252	Large	Fragment	488	72	69	27
253	Medium	Fragment	174	51	37	25
254	Medium	Fragment	177	53	46	21
255	Medium	Fragment	220	48	44	21
259	Medium	Fragment	181	57	41	20
260	Medium	Fragment	118	53	41	18
261	Medium	Fragment	207	53	36	18
267	Small	Fragment	47	29	24	22
268	Medium	Fragment	138	49	31	27
269	Medium	Fragment	127	43	29	19
270	Medium	Fragment	58	38	24	14

2. Experimental

2.1. Sampling

A sample for bulk chemical analysis, not exceeding 20 mg, was taken from each ingot by drilling using a 1 mm high speed steel drill bit. To obtain uncorroded interior sample of metal for a reliable determination of the alloy composition, the drillings of the corroded surface were discarded until shiny metal turnings appeared. The metallographic samples were taken using an Isomet diamond saw. The sections were mounted in epoxy resin, ground and then polished using diamond paste to a finish of 1 μm .

2.2. Bulk chemical analysis

The alloy composition was determined using ICP-MS and ICP-AES at the Natural History Museum, London using an Agilent 7700x ICP mass spectrometer and Thermo Scientific iCap 6500 Duo ICP spectrometer, respectively. The samples (10–20 mg for copper ingots and 4–7 mg for bronze artefacts) were weighed to ± 0.01 mg, digested in a mixture of 0.55 ml of concentrated HNO_3 and 1.75 ml of concentrated HCl (both acids SpA™ grade, ROMIL Ltd) with careful heating for a few minutes to improve dissolution of sulphide inclusions, and made up to 25 ml with ultra-pure water (cf. Hughes et al., 1976). Only sulphur (S) concentrations were determined by ICP-AES in copper ingots, the rest of the elements including copper (Cu) were determined by ICP-MS. ICP-AES was also used to determine tin (Sn) concentrations in the bronze artefacts. Based on the analysis of a certified reference material (CRM) of bronze composition (Gunmetal BAM-211) the analytical accuracy (systematic error) for arsenic (As), bismuth (Bi), lead (Pb), manganese (Mn), selenium (Se), silver (Ag) and zinc (Zn) is within the uncertainty of the certified values for the CRM (0.6–5%); for tin is within 0.2% (relative); for copper – 0.3%; nickel (Ni) – 1.5%; antimony (Sb) – 3%; iron (Fe) – 5%; cadmium (Cd) – 7%; and for sulphur is within 12%. The reproducibility of the ICP-MS determination of copper was assessed by triplicate analysis of three bronze CRMs (Gunmetal BAM-211, Bronze “C” BCS-207, Bronze BCS-183/1) and two ancient bronze samples used in this study, and was shown to be within 0.8%.

2.3. Metallography

Following the compositional analysis, metallurgical samples were taken from 10 ingots (2010,8032.100; 201; 203; 254; 255; 259; 261; 267; 269; and 270), chosen in an attempt to cover ingots with a variety of impurity levels.

Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS) was used for the study of inclusions in the metals. The SEM-EDS analysis was carried out at the British Museum using a Hitachi S-3700N Variable Pressure SEM with an Oxford INCA Energy system, running at an accelerating voltage of 20 kV at low vacuum (50 Pa) with a working distance of 10 mm. After examination of the inclusions, the polished sections were etched using alcoholic ferric chloride solution to reveal the metallographic structure of the metals.

3. Results

3.1. Chemical composition

The ICP-MS and ICP-AES analyses (Table 2) show that all analysed copper ingots were made of unalloyed copper (rather than bronze) with a mean copper content of $98.7 \pm 2.05\%$. Only three (out of 25) samples show analytical totals deviating more than 2% from 100%. The overestimated copper concentration in sample 2010,8032.261 is most probably due to a weighing error. The lowest total for sample 2010,8032.267 is due to corrosion products present in the sample, confirmed in the metallographic section taken from this ingot.

The impurity contents of the Salcombe copper ingots are generally low with maximum values for all but two elements, in addition to sulphur, being less than 0.31%. Sample 2010,8032.201 contains 1.08% antimony and sample 2010,8032.261 contains 0.64% lead. The most common trace elements of the Salcombe ingots are silver, arsenic, cobalt (Co), nickel, lead, antimony and selenium; with gold (Au), bismuth, tin and zinc also being detected in most of the samples. The iron and sulphur contents of copper can be indicative of the kind of ore and technology used to smelt it (Craddock and Meeks, 1987). Other impurities such as cobalt, nickel, arsenic, antimony, silver and bismuth have been regarded as being more indicative of the copper ore sources (Northover, 2013). Arsenic, antimony, silver and nickel have been regarded as the principal impurities in British Bronze Age bronzes (Rohl and Needham, 1998), the concentrations of these in 25 Salcombe ingots are typically low: arsenic, below 0.01% in 15 ingots and up to 0.26% in the rest of the samples; antimony below 0.05% in all but one sample; silver, below 0.08% in all but two samples; and nickel, below 0.1% in 21 ingots and up to 0.21% in the remaining four samples.

3.1.1. Sulphur

For the ingots, sulphur concentration is in the range of 0.32–0.79% with the mean being 0.59%, while for the two artefacts sulphur contents are 0.06 and 0.03%, respectively, an order of magnitude lower than those in the ingots. Detailed study of sulphide inclusions is reported below in section 3.2.

3.1.2. Iron

Compared with the other three large groups of bronze ingots the Salcombe ingots contain a much lower level of iron, below 0.02% (Fig. 3a). The iron contents in the two artefacts analysed (rapier 2010,8032.17 and palstave 2010,8032.23) are higher, being 0.15% and 0.05%, respectively (Table 2).

3.1.3. Lead

All but one Salcombe ingots analysed have a low lead content (below 0.06%). Only one ingot (2010,8032.261) contains a significant amount of lead (0.64%). The lead contents in the two artefacts analysed are higher, being 0.71% and 0.33%, respectively (Table 2). Lead distribution for all sites is not dramatically different, but lead contents in some Hertford Heath and Sardinian ingots are higher, exceeding 1%. The lead contents in the Uluburun ingots are in a narrow range between 0.01 and 0.1% (Fig. 3b).

3.1.4. Arsenic

The pattern of arsenic contents is shown in Fig. 3c. Salcombe is similar to Hertford Heath with the majority of the ingots from each site having $\leq 0.1\%$ arsenic but the highest level for Salcombe being 0.26% while for Hertford Heath being 0.95%. The pattern for the two Mediterranean sites is quite different. The arsenic contents of the Sardinian ingots have a wide distribution and are up to 0.99%, while that of the Uluburun ingots are concentrated in a narrow range with all being 0.1–0.4%. For Salcombe the arsenic contents in the two artefacts analysed are generally higher than the ingots, being 0.11% and 0.13%, respectively (Table 2).

3.1.5. Silver

The pattern of silver content distribution (Fig. 3d) is also similar for Salcombe and Hertford Heath: it has the highest probability at 0.03–0.1% and the maximum level at 0.30 and 0.36%, respectively. The silver contents of the Sardinian ingots have a wide distribution with the highest probability at 0.003–0.01% and are up to 0.67%, while silver contents of the Uluburun ingots are very low ($< 0.01\%$ in all ingots).

3.1.6. Nickel

There are little differences in the level of nickel among those four groups but Uluburun shows a different distribution of the nickel

Table 2
Bulk chemical composition of the copper ingots and artefacts.

Sample No.	Cu	S	Ag	As	Au	Bi	Cd	Co	Fe	In
	%	%	µg g ⁻¹							
<i>Copper ingots</i>										
2010,8032.100	98.5	0.607	487	4.39	7.40	< 0.5	< 0.08	32.4	111	0.41
2010,8032.101	98.7	0.408	66.6	1134	< 0.33	21.5	< 0.08	0.60	154	0.39
2010,8032.103	97.8	0.609	36.3	14.3	0.35	2.12	< 0.08	0.45	< 92	< 0.37
2010,8032.181	99.9	0.679	715	49.2	1.46	13.5	< 0.08	1.65	< 92	0.87
2010,8032.183	100.1	0.711	290	61.0	0.64	4.77	< 0.08	9.73	< 96	0.98
2010,8032.184	100.1	0.673	655	16.7	3.86	1.00	< 0.08	14.7	< 100	1.72
2010,8032.190	100.6	0.712	385	77.7	3.69	16.5	< 0.08	17.7	< 118	4.76
2010,8032.196	100.0	0.656	86.6	< 3.5	0.37	76.0	< 0.08	1.41	< 96	1.28
2010,8032.201	97.3	0.641	1220	145	< 0.33	38.6	< 0.08	6.52	< 90	2.41
2010,8032.202	99.4	0.694	529	25.1	0.54	1.61	< 0.08	3.47	< 146	< 0.37
2010,8032.203	99.6	0.565	28.8	675	< 0.33	142	< 0.08	< 0.21	< 77	1.78
2010,8032.220	98.7	0.597	16.2	193	< 0.33	1.05	< 0.08	4.56	< 100	< 0.37
2010,8032.226	99.1	0.626	440	563	4.33	7.33	< 0.08	34.5	< 74	2.30
2010,8032.232	98.0	0.631	351	32.4	0.43	4.06	< 0.08	8.61	< 104	0.99
2010,8032.252	98.8	0.615	200	47.7	17.5	14.4	< 0.08	24.5	< 134	18.2
2010,8032.253	99.4	0.621	56.4	9.42	3.00	< 0.5	< 0.08	13.1	< 115	1.12
2010,8032.254	98.2	0.481	84.9	633	< 0.33	7.42	0.15	1.64	< 95	< 0.37
2010,8032.255	98.5	0.319	621	2603	< 0.33	24.9	< 0.08	0.59	90.7	1.17
2010,8032.259	99.0	0.654	738	31.3	0.51	2.97	< 0.08	8.46	121	0.72
2010,8032.260	99.1	0.609	47.2	4.69	< 0.33	< 0.5	< 0.08	0.80	88.8	0.74
2010,8032.261	103.2	0.558	3008	86.1	2.68	6.09	2.77	2.19	101	3.34
2010,8032.267	91.3	0.427	161	1589	< 0.33	14.8	< 0.08	0.56	179	0.80
2010,8032.268	95.7	0.521	11.7	15.6	5.81	1.30	< 0.08	1.17	< 106	< 0.37
2010,8032.269	97.8	0.422	725	145	< 0.33	3.93	< 0.08	0.78	219	0.77
2010,8032.270	98.7	0.793	442	935	0.34	19.1	< 0.08	3.47	< 150	6.03
<i>Min</i>	91.3	0.319	11.7	< 3.5	< 0.33	< 0.5	< 0.08	< 0.21	< 74	< 0.37
<i>Max</i>	103.2	0.793	3008	2603	17.5	142	2.77	34.5	219	18.2
<i>Mean</i>	98.7	0.593	456	364	2.24	17.1		7.75		2.11
<i>Median</i>	98.8	0.615	351	61.0	0.43	6.09		3.47		0.98
<i>Bronze artefacts</i>										
17	86.2	0.065	587	1119	< 0.33	28.7	< 3.5	7.727	1432	< 3
23	88.0	0.033	393	1330	11.1	59.1	< 3.5	180	463	27.7
Sample No.	Mn	Ni	Pb	Sb	Se	Sn	Te	Zn	Total	
	µg g ⁻¹	%								
<i>Copper ingots</i>										
2010,8032.100	< 15	2041	115	495	44.5	< 5	< 0.24	12.7	99.4	
2010,8032.101	< 15	81.6	13.8	27.6	44.6	134	< 0.24	12.5	99.3	
2010,8032.103	< 15	47.0	14.2	153	28.6	17.2	< 0.24	7.49	98.4	
2010,8032.181	< 15	313	12.2	791	18.4	12.6	< 0.24	35.4	100.8	
2010,8032.183	< 15	831	203	52.4	17.5	11.4	< 0.24	< 7	101.0	
2010,8032.184	< 15	836	207	191	19.6	16.3	< 0.24	< 7	101.0	
2010,8032.190	< 15	427	257	189	91.3	13.6	1.36	18.5	101.4	
2010,8032.196	17.4	221	70.2	5.78	137	< 5	1.43	< 7	100.7	
2010,8032.201	17.3	1009	10.5	10752	6.53	9.87	< 0.24	17.4	99.3	
2010,8032.202	< 15	516	12.9	80.5	14.9	9.46	< 0.24	< 7	100.2	
2010,8032.203	< 15	16.5	1.71	43.9	18.2	285	< 0.24	< 7	100.3	
2010,8032.220	< 15	351	227	29.5	22.8	39.6	< 0.24	< 7	99.4	
2010,8032.226	< 15	322	38.8	13.1	19.9	8.42	6.58	8.83	99.8	
2010,8032.232	< 15	606	5.20	44.1	10.9	7.36	< 0.24	11.4	98.8	
2010,8032.252	27.8	157	89.2	51.4	190	16.6	2.54	16.4	99.5	
2010,8032.253	< 15	1076	6.49	53.0	8.38	6.82	< 0.24	11.4	100.2	
2010,8032.254	< 15	429	599	357	25.8	166	< 0.24	< 7	98.9	
2010,8032.255	< 15	140	86.3	295	53.0	292	0.555	< 7	99.2	
2010,8032.259	< 15	882	13.7	72.9	35.8	18.5	< 0.24	< 7	99.8	
2010,8032.260	< 15	545	2.71	61.8	3.91	< 5	< 0.24	< 7	99.7	
2010,8032.261	< 15	228	6417	489	27.7	< 5	< 0.24	936	104.8	
2010,8032.267	< 15	164	604	427	199	20.2	0.322	< 7	92.0	
2010,8032.268	< 15	242	2.73	3.13	48.5	< 5	16.8	< 7	96.3	
2010,8032.269	21.3	339	214	462	4.58	8.65	< 0.24	< 7	98.4	
2010,8032.270	< 15	1418	82.5	109	381	49.7	4.34	< 7	99.8	
<i>Min</i>	< 15	16.5	1.71	3.13	3.91	< 5	< 0.24	< 7		
<i>Max</i>	27.8	2041	6417	10752	381	292	16.8	936		
<i>Mean</i>		530	372	610	58.9	46.7				
<i>Median</i>		351	70.2	80.5	25.8	12.6				
<i>Bronze artefacts</i>										
17	46.1	151	7104	77.4	< 3.3	115775	< 6	18.9	98.9	
23	18.4	2261	3300	750	4.5	98066	< 6	22.5	98.8	

Table 3
Bronze Age copper ingots in Britain as determined by compositional analyses.

	Site	No of analyses/Analytical techniques	References
1	Heathery Burn, Co. Durham	1/AAS	Rohl and Needham, 1998
2	Gilmonby, Co. Durham	2/EPMA	Coggins and Tylecote, 1983
3	Beeston Regis, Norfolk	4/AAS	Lawson, 2014
4	Stuntney, Cambridgeshire	2/Optical Spectroscopy	Brown and Blin-Stoyle 1959 a & b
5	Reach Fen, Cambridgeshire		Northover, unpublished
6	Rook Hall, Essex	40/EPMA	Brown et al., unpublished
7	Wickham Bishops II, Essex	13/EPMA	Brown et al., unpublished
8	Hertford Heath, Hertfordshire	26/AAS	Craddock and Tite 1979
9	Hanningfield, Essex	3/EPMA	Brown et al., unpublished
10	Watford, Hertfordshire		Ignacio Montero pers. comm.
11	Vange, Essex	53/EPMA	Brown et al., unpublished
12	Mucking, Essex	3/EPMA	Northover, 2016
13	Stoke Hoo, Essex	4/EPMA and 1/AAS	Rohl and Needham, 1998
14	Boughton Malherbe, Kent		Lois Armada, pers. comm
15	Cliff's End, Kent	5/EPMA	Northover 2014
16	Wickham Park, London	1/AAS	Rohl and Needham, 1998
17	City (St Thomas), London		Northover, unpublished
18	Fairfield St, London		Northover, unpublished
19	Thames Bank, London		Northover, unpublished
20	Runnymede Bridge, Berkshire	7/AAS	Hook, 1988
21	Pettors Sports Field, Egham, Surrey	4/AAS	Craddock et al., 1990
22	Weston Wood, Surrey	1/EPMA?	Tylecote 1976
23	Stogursey, Somerset		Northover, unpublished
24	Gitisham, Devon		Northover, unpublished
25	Mountbatten, Devon	1/EPMA	Northover, 1988b
26	Freshwater West, Pembrokeshire	20/EPMA	Northover, unpublished
27	Porthcothan, Cornwall	6/EPMA	Northover, unpublished
28	Truro College, Cornwall	3/EPMA	Northover, unpublished
29	Gilian, Cornwall	1/EPMA?	Tylecote 1976
30	St Erth I and II, Cornwall	25/EPMA	Northover, unpublished
31	St Michael's Mount, Cornwall	8/ICP-MS	Young, 2015

contents from the other three groups with the majority concentrating in between 0.01 and 0.05% (Fig. 3e).

3.1.7. Antimony

Analytical data for antimony are only available for three groups: Salcombe, Hertford Heath and Uluburun (Fig. 3f). The two British sites show similar patterns, while the majority of Uluburun ingots show more uniformity, concentrating at around 0.01%.

3.1.8. Cobalt

Complete analytical data for cobalt are only available for Salcombe and Uluburun (Fig. 3g). Cobalt determination was not performed in a third of Sardinian ingots so we decided to exclude this element for comparison with Sardinia. The Salcombe ingots contain very low levels of cobalt (all below $35 \mu\text{g g}^{-1}$), while the Uluburun ingots all contain above $50 \mu\text{g g}^{-1}$ with a median value of $130 \mu\text{g g}^{-1}$.

3.1.9. Selenium and tellurium

Selenium concentration in the Salcombe ingots varies from 3.9 to $381 \mu\text{g g}^{-1}$ (in ingot 2010,8032.270) and tellurium (Te) was only detected in a few samples with the maximum value being $16.8 \mu\text{g g}^{-1}$ (Table 2). These elements were not sought in the analyses of the Hertford Heath ingots. A few analyses were reported on ingots from Sardinia with the maximum level being $142 \mu\text{g g}^{-1}$ and $163 \mu\text{g g}^{-1}$ for selenium and tellurium, respectively (see Table 1 in Begemann et al., 2001). Selenium and tellurium were detected in Uluburun ingots with the maximum level being $520 \mu\text{g g}^{-1}$ and $250 \mu\text{g g}^{-1}$, respectively (Table 2 in Hauptmann et al., 2002). Rehren and Northover (1991) have reported that selenium and tellurium mostly concentrate within sulphide inclusions and can be easily detected by EPMA. The analysis of Salcombe ingots appears to be consistent with the results of Rehren and Northover (1991) who found that selenium and, especially, tellurium are relatively low in sulphide inclusions in the plano-convex ingots of the British Late Bronze Age, with tellurium being always below

detection limit of EPMA ($< 0.08\%$), comparing with the oxhide ingots from Sardinia or Crete.

3.1.10. Other elements

Gold concentration in the ingots and the artefacts does not exceed $17.5 \mu\text{g g}^{-1}$, which is consistent with less than $20 \mu\text{g g}^{-1}$ of gold generally found in copper minerals (Patterson, 2017). Wayman et al. (1985) argued that smelted copper can be distinguished from native copper based, among other parameters, on extremely low concentration of gold ($< 0.025 \mu\text{g g}^{-1}$) in the latter.

The concentration of zinc is below $35.4 \mu\text{g g}^{-1}$ in the bronze artefacts and all copper ingots except 2010,8032.261, which contains $936 \mu\text{g g}^{-1}$ of zinc and $2.77 \mu\text{g g}^{-1}$ of cadmium. The same ingot also contains much higher amounts of lead and silver than the rest of analysed Salcombe ingots. It is probably smelted from the ore containing significant levels of sulphide minerals such as galena and sphalerite (Schwartz, 2000). Indium concentration does not seem to follow any particular pattern, for example, there is no correlation with zinc, which might reflect the extremely wide range of indium concentrations in indium-carrying ore minerals from the same deposit (Schwarz-Schampera and Herzig, 2002).

3.2. Microstructure

Samples with variable impurity contents were selected for metallographic study to identify any phases containing impurities. All of the samples examined were covered with corrosion products on the surface but have unaltered metal remaining in the centre. The metal appeared to be quite dense with little porosity.

All samples examined using SEM-EDS were found to contain abundant copper sulphide inclusions with low iron content ($< 0.1\%$) in the inclusions, while copper oxides were not found in any of the samples selected for microanalysis. These findings indicate that the copper ores used for producing the ingots were more likely rich in copper sulphides

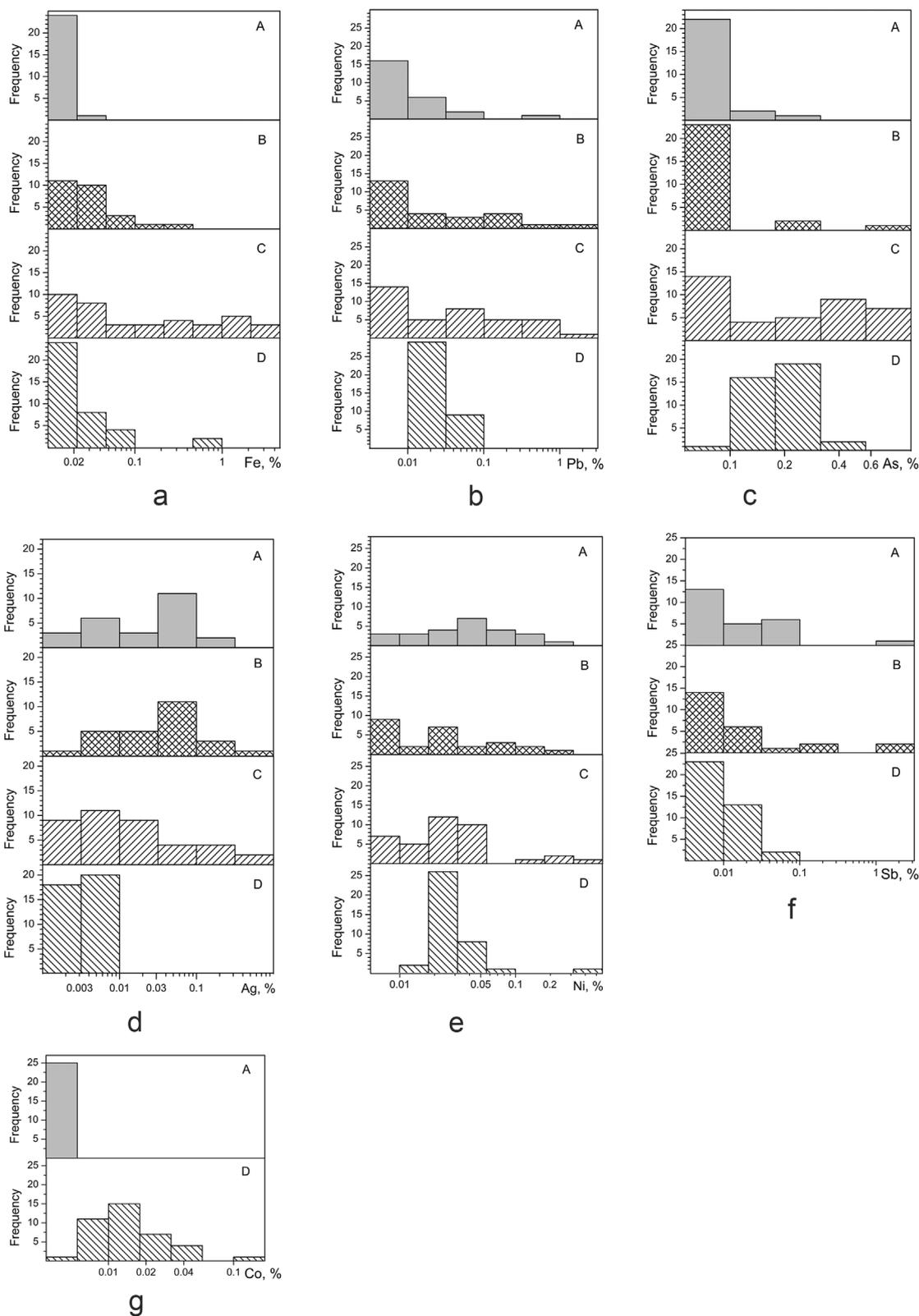


Fig. 3. Histograms of trace element concentrations in copper ingots from four sites (three sites for antimony and two sites for cobalt). A – Salcombe; B – Hertford Heath; C – Sardinia; D - Uluburun.

rather than copper-iron-sulphides, such as chalcopyrite if sulphide copper ores were indeed used for production of the ingots.

Bulk sulphur contents of the Salcombe ingots were found to be 0.32–0.79% by ICP-AES (Table 2) and the sulphur content calculated from the area of sulphide inclusions using SEM images was 0.57–1.05%.

Sulphur contents quoted in most publications (Ryndina et al., 1999; Craddock, 1988) were by SEM-EDS, hence not necessarily directly comparable with the true bulk data reported here, especially as exact protocols for SEM-EDS map area calculations are seldom reported. Sulphur has been reported to be the most abundant impurity in

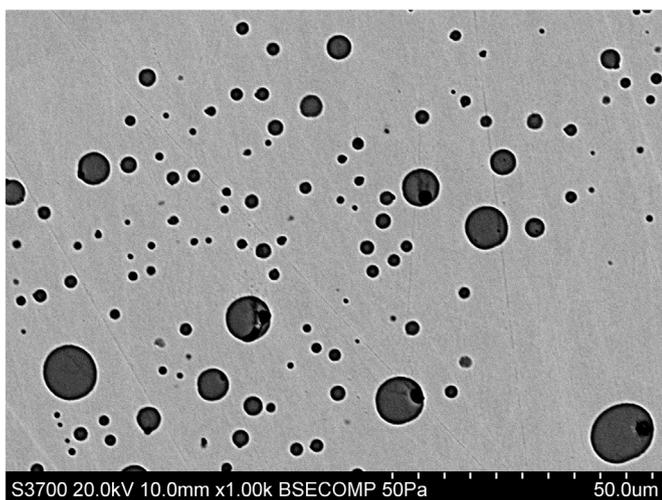


Fig. 4. SEM image of sample 2010,8032.100, showing sulphide inclusions (dark globules) without other impurities.

hundreds of ingots found in Essex hoards with all but three having a content of $\geq 0.5\%$ (Brown et al., unpublished) as measured by EPMA, which accuracy is dependent on the particle size and spacing of the inclusions analysed.

After etching, all the samples studied showed granular structures, ranging from equi-axed to long columnar grains, as expected in cast copper.

Sample 2010,8032.100, which has the highest bulk concentration of nickel (0.20%), does not have other impurities detected by SEM-EDS in the copper. Because nickel and copper are completely soluble in each other, only sulphide inclusions, some of which contained lead, were found in this ingot (Fig. 4).

In sample 2010,8032.259, inclusions other than copper sulphides are present, which were found to contain lead or lead and tin with some arsenic and antimony. In sample 2010,8032.254, although no impurities are present at particularly high levels, lead-rich and arsenic-, antimony- and tin-rich particles were found to be present in sulphide inclusions (Fig. 5).

In sample 2010,8032.201, which contains 1.08% antimony, antimony-rich grains were found within some of the copper sulphide inclusions, as well as silver and antimony-rich phases in the metal (Fig. 6).

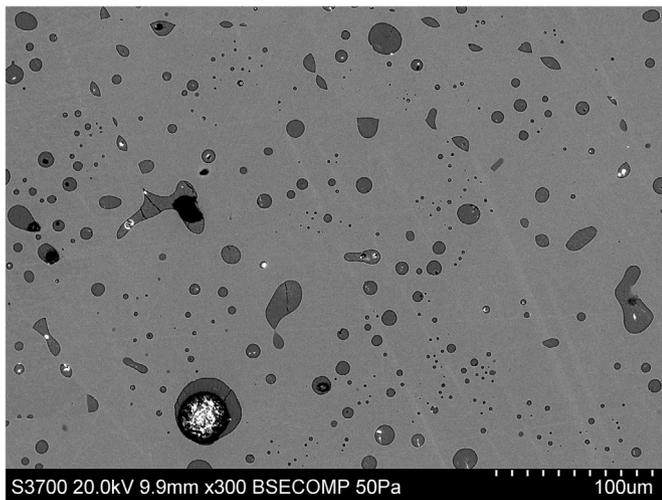


Fig. 5. SEM image of sample 2010,8032.254, showing lead-rich and arsenic-, antimony- and tin-rich particles (bright spots) present in sulphide inclusions, though no impurity was found at particularly high levels by ICP-MS.

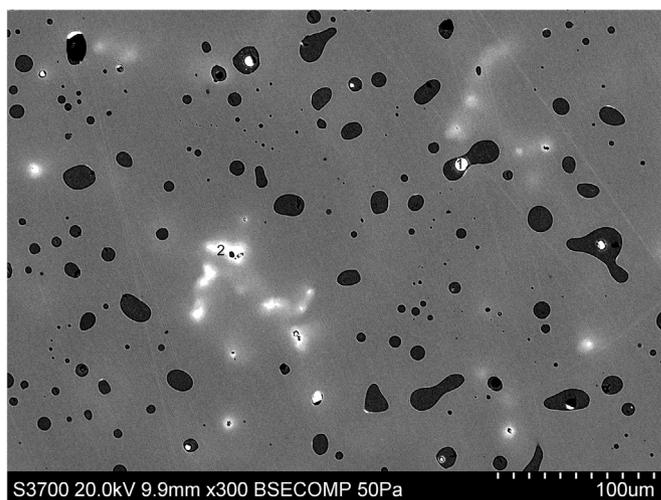


Fig. 6. SEM image of sample 2010,8032.201, showing antimony oxides within sulphide inclusions (1) and silver and antimony-rich phases in the metal (2).

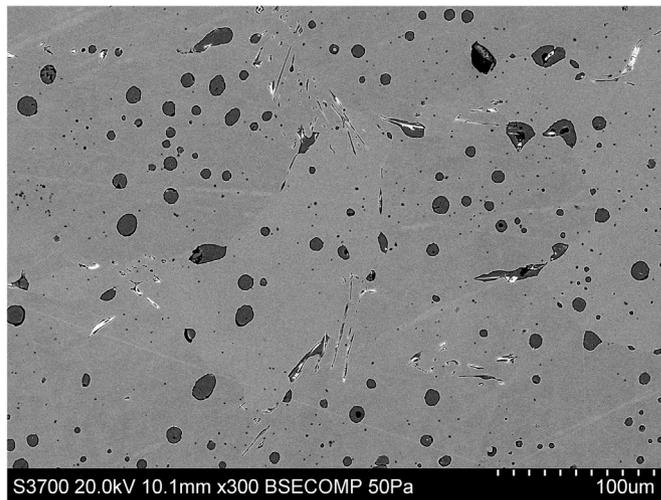


Fig. 7. SEM images of sample 2010,8032.255, showing cassiterite crystals (bright needles) present in sulphide inclusions and in the metal.

Sample 2010,8032.203 and 2010,8032.255 were found to contain 0.029% tin in the bulk composition. The microstructures showed rhomboid or elongated grains (5–20 μm on the longer axis) with tin and oxygen present in both samples (Fig. 7), indicating that tin is probably present as cassiterite. Unreacted cassiterite particles were reported by Wayman et al. (1988) in slag produced by experimental bronze production from cassiterite and copper, and also in bronze ingots produced by scrap melting of leaded bronzes in their experimental casting, with the latter being due to over-oxidation of recycled bronzes (Northover, 1988c). Angular tin oxide inclusions were reported to be present in a copper ingot containing 1.2% tin found off Plymouth, Devon and attributed to either residual cassiterite used in melt or oxidation products of recycled bronzes (Meeks, 1990). However, both Northover (1988c) and Meeks (1990) misinterpreted experimental results produced by Wayman et al. (1988) on using cassiterite in melt. It is difficult to interpret the presence of such a low level of cassiterite in the Salcombe ingots; neither cassiterite nor recycled bronzes were likely used for the ingots. Numerous grains containing bismuth as the only detectable metal component or bismuth with lower amounts of tin, arsenic and antimony were observed in the metal matrix of sample 203 (only 0.014% bismuth in the bulk composition). Inclusions in sample 255 are only copper sulphide and tin oxide, apart from a few grains containing high levels of lead with some arsenic and antimony. Although samples

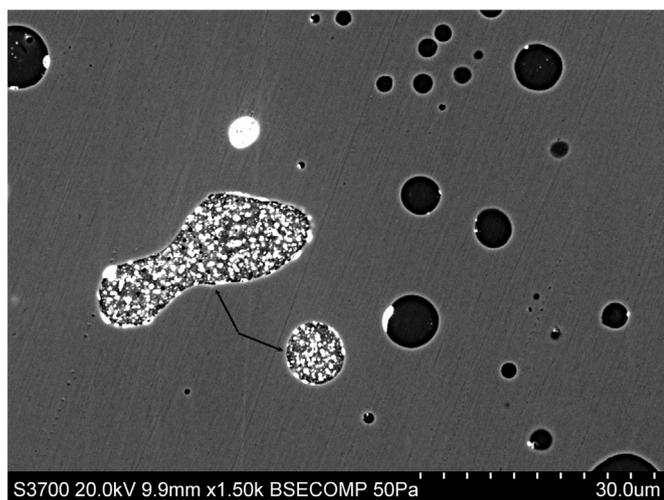


Fig. 8. SEM image of sample 2010,8032.261, showing the presence of sulphide inclusions (dark globules), lead globules (the brightest particles), and lead and silver-rich inclusions (indicated by arrows).

203 and 255 both contain cassiterite crystals, they are very distinct by their levels of bismuth, antimony, lead and arsenic, so they are not likely to represent the same melt of metal.

Sample 2010,8032.261 has the highest silver, lead and zinc concentrations among the samples analysed: 0.30%, 0.64% and 0.09% in the bulk samples, respectively. It also contains a trace amount of cadmium, which is below the detection limit in 23 out of 25 samples analysed (Table 2). The microstructure (Fig. 8) shows that the silver and lead-rich phases are present in the metal rather than within sulphide inclusions, while tiny lead particles are present in some of the sulphide inclusions. Even though antimony was detected by SEM-EDS in some of the heavy metal inclusions, its bulk concentration in the sample is only 0.049%. Both the bulk composition and the microstructure suggest that this ingot differs significantly from the other ingots.

Sample 2010,8032.267 contains 0.16% arsenic, 0.06% lead, 0.04% antimony and smaller amounts of other impurities in the bulk composition. Arsenic-, lead- and antimony-rich particles are present in the microstructure, with most of them being within the sulphide inclusions. Despite of a low bulk concentration of $20 \mu\text{g g}^{-1}$, tin was also detected in some of these particles.

The microstructure of sample 2010,8023.269, containing $725 \mu\text{g g}^{-1}$ silver, $214 \mu\text{g g}^{-1}$ lead and $462 \mu\text{g g}^{-1}$ antimony in bulk composition, shows the presence of lead- and antimony-rich particles in some of the sulphide inclusions. Sample 2010,8032.270 containing 0.14% nickel, $935 \mu\text{g g}^{-1}$ arsenic and $82.5 \mu\text{g g}^{-1}$ lead in bulk composition was found to have a few lead- and arsenic-rich particles present in the sulphide inclusions.

4. Discussion

4.1. Copper production

There is currently no evidence for Middle-Late Bronze Age (c. 1600–800 BC) copper mining or smelting in southwest England, despite (or perhaps due to) the very extensive copper ore sources in the region. The copper ore sources were heavily exploited up until the 20th century leaving primarily circumstantial evidence of prehistoric mining activity (Budd and Gale, 1994; Craddock and Craddock, 1996). The evidence for Early Bronze Age (c. 2200–1600 BC) copper extraction in southwest England comprises the dating of possible copper mining to c. 1950–1750 BC at Roman Lode, Exmoor (Juleff and Bray, 2007) and the

compositional analyses of copper-alloy objects by Bray and Pollard (2012). The recent comprehensive environmental analyses of tin, lead and copper levels within undisturbed peat bogs on Dartmoor and Bodmin Moor did not detect any Bronze Age copper extraction (Meharg et al., 2012). Copper oxides were not identified in the microstructure of any of the samples analysed, suggesting that these ingots were probably not from re-melting primary smelting lumps. As Tylecote (1976) found, re-melting must have been done under quite oxidising conditions, generating copper oxides, especially penetrating along the grain boundaries. Tylecote believed that the ingots had formed in the base of the smelting furnace and represented the primary product. However, primary copper ingots are often of high porosity in microstructure, but the copper from Salcombe appeared to be of excellent density, pointing to the product of refining and re-casting operations in reducing conditions. In contrast, the Uluburun ingots with a high porosity point to a primary smelting product; but cuprite present in the metal indicates the product of re-melting and re-casting (Hauptmann et al., 2002). Therefore, it is inconclusive how the Salcombe ingots were made; they could be the product of either primary smelting process or refining and re-casting operations.

Sulphur is practically insoluble in molten copper and is separated in a form of copper sulphide inclusions even at low bulk concentrations ($< 0.1\%$) in a copper object (Chernykh et al., 1998). Oxide copper ores may contain significant amounts of sulphur either as impurities in copper carbonates or residual unaltered sulphides and sulphur can concentrate (in a form of sulphide inclusions) in copper smelted from oxide ores (Tylecote, 1976). Craddock (1988) reported that sulphur contents of metal produced from malachite ores in Timna vary from 0.1 to 0.5% (except one with 0.8%). Therefore, the presence of copper sulphide inclusions and/or moderate bulk concentrations of sulphur in copper ingots do not necessarily point to sulphide ores being the source of metal and may not provide convincing evidence of the type of ore used for smelting (Balmuth and Tylecote, 1976; Chernykh et al., 1998). The experimental smelting, however, undertaken by Tylecote et al. (1977) proved that matte smelting and roasting of sulphide copper ores caused a major loss of volatile impurities and so would produce a mainly low impurity copper. Brown et al. (unpublished) claimed in their report on Essex hoards that sulphide ores rather than oxide ores were likely used for the copper ingots based on the high sulphur concentrations in the metal and the quantity of matte in the slag entrapped in the surfaces of some ingots. Brown et al. (unpublished) speculated that the very low iron contents ($\leq 0.022\%$) in copper ingots from the Essex hoards could simply indicate that copper was smelted in such a way that iron was not reduced, because a significant amount of magnetite was found in the surface slag inclusions. Experiments of primary smelting of copper-iron-sulphide minerals e.g. chalcocite Cu_2FeS_2 or bornite Cu_5FeS_4 , however, proved difficult and the copper produced was found to contain substantial amounts of iron (0.5–5%) (Craddock et al., 2007). Although it is possible that iron-free copper minerals chalcocite Cu_2S or covellite CuS could have been the source for these copper ingots as this would explain the very low level of iron in the ingots (not exceeding 0.022%), smelting from oxide (carbonate or silicate) ores could also be an explanation as these ores are generally more readily available.

Some fluctuations in impurity levels revealed by bulk chemical analysis were also noticeable in the microstructural investigation as mentioned above. Although the variations in the composition may be due to differences in ore mineralogy, it is impossible to reconcile these ingots with a single source or region, as different sources of similar ore type could have been exploited simultaneously, resulting in similar chemical compositions (Rohl and Needham, 1998). Ingot 2010,8032.201, containing over 1% antimony, was probably produced from fahlerz ores. Lead isotope measurements in combination with the chemical analyses would increase the chances of identifying possible sources.

4.2. Copper ingots

There are currently 31 sites in Britain which have yielded Bronze Age copper ingots which have a relatively secure archaeological context and have been confirmed compositionally by archaeometallurgical analyses (Fig. 1, Table 3). They are relatively tightly restricted in space and time with no Bronze Age copper ingots known beyond the Late Bronze Age (c. 1150–800 BC), specifically the Ewart Park metalwork phase (c. 1000–800 BC) (Roberts et al., 2013), and very few outside of the coastal and estuarine areas of southern England (Fig. 1, Table 3). This quantity of sites and copper ingots is relatively small when compared to Late Bronze Age metalwork finds known from across England and Wales. For instance, 142 Late Bronze Age (c. 1150–800 BC) metalwork hoards comprising 3403 copper or copper alloy objects have been recorded in the last 15 years alone (Wiseman, 2018). This is a direct consequence of the legal requirement in England and Wales since 2002 under the Treasure Act (1996, amended 2002) to report terrestrial discoveries of prehistoric base-metal hoards. However, even before this revolutionary legal requirement (see Murgia et al., 2014), Huth (1997) had recorded 312 Late Bronze Age copper or copper alloy metalwork hoards in England alone that had been found up until 1990. The identification of plano-convex or bun ingots and ingot fragments in many Late Bronze Age (c. 1150–800 BC) hoards in Britain has rarely led to compositional analyses. Scholars have typically assumed that these ingots and ingot fragments are bronze on the basis of the associated bronze tools, weapons and ornaments. However, the compositional analyses of large ingot assemblages in terrestrial hoards as at Boughton Malherbe and Freshwater West (Table 3) as well as the maritime assemblage at Salcombe (Table 2) demonstrate that the numbers of Bronze Age copper ingots have been severely underestimated. This conclusion is strongly supported by recent and comparable research in northwest France (Le Carlier et al., 2014) and western Germany (Bachmann et al., 2002/2003).

4.3. Impurity patterns of copper ingots from different sites in Britain

Comparing the two large groups of ingots from Britain (Salcombe and Hertford Heath), it can be seen that they have a similar impurity pattern for lead, silver, arsenic, nickel and antimony (Fig. 3). The major difference in composition between the two British sites is the iron contents, which range 0.03–0.16% in the ingots from Hertford Heath but are lower in Salcombe ingots ($\leq 0.02\%$).

Smaller numbers of analyses by AAS, ICP-AES and ICP-MS are available on bun ingots from other sites in Britain (Table 4). Although not suitable for plots in Fig. 3 they may provide information on similarity/difference between sites. Eight ingots from St Michael's Mount in Cornwall, analysed using ICP-MS, show apparently higher levels of tin, silver and iron (Young, 2015) than the Salcombe ingots. Seven ingots from Runnymede Bridge, Berkshire (of the Ewart Park Assemblage), analysed by Hook (1988) using AAS and published by Rohl and Needham (1998) show similar impurity patterns to that of the Salcombe ingots except for iron. The iron contents in these samples are in the range of 0.02–0.18%, similar to ingots from Hertford Heath. Four ingots from Petters Sports Field, Surrey (Craddock et al., 1990) show a similar impurity pattern to the Salcombe ingots, i.e. with all impurities present at very low levels. Four Late Bronze Age bun ingots from the Beeston Regis Hoard (No. 21 & 28 from Hoard I and No. 10 & 11 from hoard II), Norfolk analysed by Craddock et al. and published in Lawson (2014) showed that three of them (not No. 28) were unalloyed copper with similar trace element patterns to those of the Salcombe ingots.

Though analysed only by EPMA, the copper ingots from Essex hoards appeared to be quite pure with a few exceptions containing one or more impurities of $\geq 0.5\%$. The Essex ingots showed little difference in impurity pattern from the Salcombe ingots except for arsenic, which appeared generally higher than that in the Salcombe ingots. However, it is not known if this reflects a real difference in arsenic concentrations or

Table 4
Range of trace element concentrations in ingots from some sites in Britain.

Sites	Sample size	Pb (%)	Sn (%)	Ag (%)	Fe (%)	Sb (%)	Ni (%)	As (%)
Salcombe, Devon (Table 2)	25	< 0.06 but one (0.64)	< 0.01 but four (0.029)	< 0.3; mostly < 0.05	< 0.022	< 0.08 but one (1.075)	< 0.204	< 0.26
Hertford Heath, Hertfordshire ^a	24	< 0.01–0.50 (one 1.2)	< 0.40	0.005–0.26	0.007–0.29	< 0.2 but two (1.2; 1.3)	0.003–0.18	< 0.2 but one (0.95)
St Michael's Mount, Cornwall ^b	8	< 0.06 but one (0.64)	0.009–0.638	0.039–0.937	0.012–0.471	< 0.02 but one (0.285)	< 0.130	< 0.18 but one (1.349)
Runnymede Bridge, Berkshire ^c	7	< 0.1 but one (0.69)	nd	0.005–0.009	0.09–0.179	< 0.056	< 0.156	< 0.489
Petters Sports Field, Surrey ^d	4	< 0.1	< 0.04	< 0.04	0.01–0.03	< 0.08	< 0.06	0.1–0.2
Beeston Regis hoard, Norfolk ^e	3 (excluding a Cu-Pb ingot)	< 0.035	< 0.07	< 0.06	< 0.02	< 0.03	< 0.085	< 0.08

Notes.

^a Craddock and Tite, 1979.

^b Young, 2015.

^c Hook, 1988; Rohl and Needham, 1998.

^d Craddock et al., 1990 (Table 3, P78).

^e Lawson, 2014.

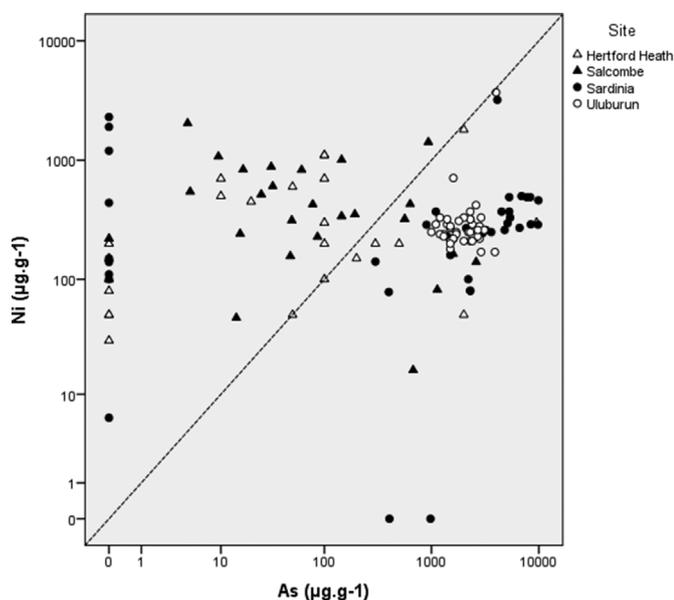


Fig. 9. Nickel versus arsenic in the bun ingots from four different regions (those in line with 0 represent samples below detection limits of the elements).

is due to a higher detection limit of arsenic by EPMA.

4.4. Nickel versus arsenic

It has been reported by Northover (2013) that for Middle and Late Bronze Age metalwork from northwest Europe the most significant impurities were arsenic and nickel and the arsenic-to-nickel ratios showed regional differences and also chronological changes. Fig. 9 shows that $Ni > As$ in the majority of the ingots from Salcombe and Hertford Heath. Four of the Hertford Heath ingots (shown on the line of 0% As) have an arsenic content below the detection limit of 0.005% (see Craddock and Tite, 1979). This trend of arsenic-to-nickel ratios for the Salcombe ingots is consistent with analytical results of 30 pieces of bronze artefacts or fragments (but not ingots) of the pre-2005 finds from the Salcombe sites by Northover (2013). Runnymede Bridge also shows a similar pattern of arsenic-to-nickel ratios, i.e. $Ni > As$ in five out of seven samples (Hook, 1988; Rohl and Needham, 1998). In contrast, the Uluburun ingots show a very uniform arsenic-to-nickel ratio, all being $Ni < As$. The majority of the Sardinian ingots are also uniform and have $Ni < As$. Those Sardinian ingots with 0% arsenic and nickel present samples below detection limits, which were likely 0.02% and 0.005 judging by data published in Maddin and Merkel (1990). Therefore, some of the Sardinian samples in line with 0% As could be on the other site of the $X = Y$ line, i.e. with $Ni < As$. In summary, the bun ingots from the Mediterranean region (Sardinia and Uluburun) are generally of $Ni < As$ (Fig. 9), in opposite trend to that of the British bun ingots. The exception are the ingots from St. Michael Mount, which show $Ni < As$ in seven out of eight samples (Young, 2015) suggesting that they may have been imported from other regions. The sample sizes of other sites, e.g. Petters Sports Field and Beeston Regis Hoard are too small to be comparable.

The Salcombe ingots show a distinctly different impurity pattern, especially for lead, arsenic, silver and nickel, from the Uluburun ingots and differ in impurity patterns of iron and arsenic from the Sardinian ingots (Fig. 3). The arsenic-to-nickel ratios (Fig. 9) suggest that the British copper might potentially reflect more than one source of ore, while Uluburun has a uniform composition. Compared with Uluburun, the Sardinian copper ingots vary in composition but the variation is smaller than the British copper ingots. The connection with Sardinian copper cannot be entirely excluded for some Salcombe ingots as a Sicilian type object (Fig. 4.6 in Needham et al., 2013) was present in the

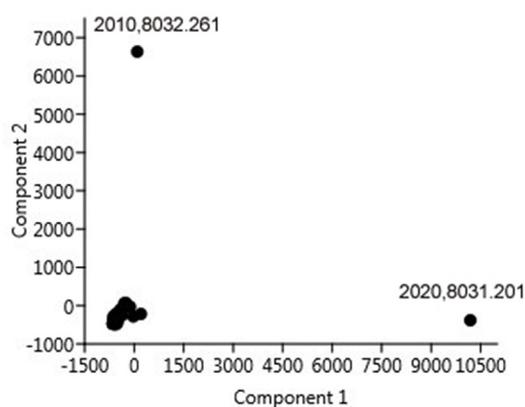


Fig. 10. PCA plot of the chemical analysis of the Salcombe ingots, showing two outliers - 2010,8031.201 with 1.08% Sb and 2010,8032.261 with elevated concentrations of Pb, Ag, Zn and Cd.

earlier discoveries at Salcombe. The majority of the ingots are generally consistent in their composition with very pure copper sources in England and Wales (Ixer and Budd, 1998). However, two of the ingots (201 and 261) that are compositional outliers according to multivariate statistical analysis (Fig. 10) might have come from different sources than the rest. Sulphur is excluded from the plot, as its concentration does not really reflect the copper ore sources. It is not surprising that the Salcombe copper ingots could have come from more than one source, as multiple sources for copper ingots from Essex hoards were identified based on the ratios of selenium and tellurium in sulphide inclusions and confirmed by lead isotope analysis (Brown et al., unpublished).

Although it is not possible to identify the sources of copper ore used for the ingots based merely on the chemical compositions, the very low concentration of iron in all the Salcombe ingots analysed would seem to exclude many of the central European and Alpine sources where more advanced slagging smelting processes had been in use since at least the Middle Bronze Age resulting in higher iron contents (in the range of $mg\ g^{-1}$) (Craddock, 1999, 2009). The very low level of iron in the Salcombe ingots suggests that they were produced by the primitive smelting process which was in use up to the end of the Bronze Age at least in much of Europe (Craddock and Meeks, 1987) but it is difficult to explain the excellent density of the ingots, as mentioned above.

4.5. Comparing ingots with artefacts from the Salcombe site

Bronze artefacts from the pre-2005 Salcombe finds were analysed by Northover (2013) using EPMA. Although the spatially resolved analytical data (e.g. by EPMA) are not directly comparable with the bulk elemental concentrations (e.g. by ICP-AES or ICP-MS), comparison of the analytical data of the artefacts with that of the ingots may provide insight into any association between the ingots and artefacts.

The two bronze artefacts we analysed with the ingots did not seem to differ significantly from the ingots in trace element pattern apart from the contents of iron, sulphur, lead and arsenic (Table 2). Actually only iron and sulphur contents of EPMA results can be compared with that of the ICP-AES and ICP-MS results, as the rest of the EPMA data are too close to the detection limit, therefore may not be very reliable. The sulphur contents of the ingots are apparently higher than that of the bronze artefacts (including those two analysed in the current study by ICP-AES and ICP-MS, see Table 2), while the iron content shows the opposite trend, i.e., higher in most of the artefacts than in the ingots (Fig. 11). The higher iron content present in the artefacts could perhaps have been from tin (rather than copper) (Craddock et al., 2007), however our analyses of tin ingots from Salcombe showed that the iron content in them (Wang et al., 2016a) is generally not higher than in the

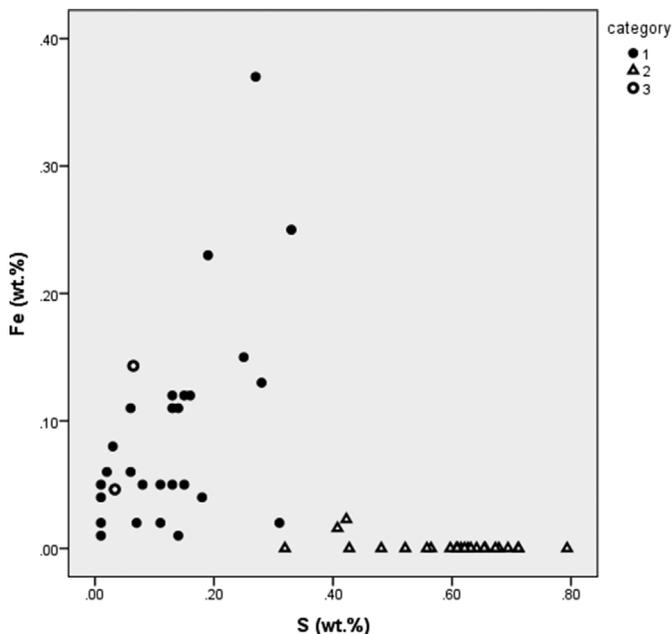


Fig. 11. Iron versus sulphur in the Salcombe objects, including bun ingots and artefacts.

1: bronze artefacts from pre-2005 finds by EMPA (Northover, 2013); 2: copper ingots from post-2005 finds by ICP-AES and ICP-MS; 3: bronze artefacts from post-2005 finds by ICP-AES and ICP-MS.

copper ingots studied here. The lower sulphur contents of the bronze artefacts could have been the result of refining of the ingots if they were used in the making of the artefacts. However, the bronze artefacts may have not been produced using these ingots. It appears unusual for bronze artefacts to have concentrations of impurities such as arsenic, antimony and nickel which match the ingots they are associated with, e.g. from the same sites (Brown et al., unpublished; Northover, 2013; Paul Craddock, pers. comm.). This has also proved true for Iberian Peninsula (Ignacio Montero Ruiz, pers. comm.). More analytical data is

required to understand whether the artefacts were produced using the ingots found at the Salcombe site.

4.6. Importance of the Salcombe copper ingots

The sample of 25 randomly selected ingots from the Salcombe seabed assemblage of 280 plano-convex ingots and ingot fragments revealed that all 25 were made from unalloyed copper with low levels of impurities. On the basis of these results, it seems very likely that the remaining 255 plano-convex ingots and ingot fragments are also unalloyed copper. Whether copper or copper alloy, the Salcombe assemblage is the largest discovery of measured both by total weight and by quantity, of Bronze Age copper plano-convex ingots in northwest Europe – even without the accompanying tin ingots. The copper ingots vary in size and weight. Although they are generally bun-shaped, the majority of the ingots are of irregular shape with smooth edges of variable thickness. The forms of the copper ingots invariably contrast sharply with the forms of the tin ingots, especially when more complete examples are compared (Fig. 12). The recent analysis of Late Bronze Age copper and copper alloy plano-convex ingot morphology in northwest France highlighted the distinctions in form between ingots cast in moulds, crucibles and in sand/earth (Le Carlier et al., 2014). The forms of the Salcombe ingots indicate that whilst the tin ingots were likely cast in sand/earth (Wang et al., 2016a), the copper ingots were likely cast in shallow ceramic moulds.

Recent debates have highlighted the importance of identifying and understanding the patterns and mechanisms for the breaking and fragmenting of plano-convex ingots (e.g. Modl, 2010; Nessel, 2014). Whilst the maritime depositional environment has undoubtedly smoothed any edges and thus prevents any straightforward attempt at re-fitting, it is possible to infer the presence or absence of copper plano-convex ingot fragmentation. Tylecote (1976) suggested that plano-convex ingot fragments could have been made by heating up the whole ingot in a fire until near its melting points, and then breaking it into several pieces; this process was probably assisted by the existence of a large amount of cuprous oxide. The absence of cuprite inclusions in the Salcombe copper ingots, however, suggests that those with irregular shapes were unlikely to be the result of the breaking into fragments.



Fig. 12. Copper (top four) and tin ingots from the Salcombe site. © Southwest Maritime Archaeology Group.

Furthermore, no sign of breaking, e.g. strain lines caused by hammering, as observed in the Early Bronze Age copper ingots from Toormore, southwest Ireland (O'Brien et al., 1989/1990), was observed in the Salcombe ingots.

There are two major implications of this analysis of the Salcombe copper ingots for understanding the Bronze Age metals trade in northwest Europe. Firstly, it provides extensive and direct evidence of the production and movement of a distinctive copper and tin trade in northwest Europe. This is contrary to the widely accepted model that virtually all Middle-Late Bronze Age metalwork (c. 1600–800 BC) in Britain was largely either recycled from older bronze or imported as scrap bronze from continental Europe as demonstrated by the Langdon Bay, Kent, southeast England shipwreck assemblage (Needham et al., 2013). It should be noted that the contemporary production of bronze swords, shields and cauldrons from c. 1300–800 BC in Britain would each have required distinctive and specific tin-copper proportions (Colquhoun and Burgess, 1988; Gerloff, 2010; Uckelmann, 2012; Wang et al., 2016b). However, the tin-bronze production processes used could, in addition to the copper and tin ingots, have included co-smelting and cementation.

Secondly, whilst both copper and tin ingots conform broadly to a plano-convex ingot form, there is no evidence for standard sizes or weights (Table 1). In addition, the metals appear to have been cast using different methods with the copper ingot fragments potentially being found in their unbroken form. This absence of a standard weight or size is despite the presence in the Salcombe assemblage of two copper alloy rectanguloid blocks which are thought, on the basis of central European parallels, to be directly associated with weighing (Needham et al., 2013, 89; Wang et al., 2016a, 89). It would therefore seem probable that the deliberate breaking of the ingots would have occurred later on, potentially when they were exchanged.

No surviving evidence for any Bronze Age boat at Salcombe site has been found. It can only be assumed that either contemporary sewn plank vessels such as found at Ferriby, northeast England (Wright et al., 2001; Van de Noort et al., 2014) or Dover, southeast England (Clark, 2004), or log boats as found at Carpow, southeast Scotland (Strachan, 2010) were involved in transporting the objects recovered. The locations of the departure and destination are unknown with the debate complicated by the high probability that two temporally distinct Bronze Age shipwrecks can be identified at Salcombe. The evidence for the intensity and sophistication of maritime movement throughout northwest Europe (Lucas Pellicer and Gomez-Ramos, 1993; Van de Noort, 2006; Robinson, 2013) cautions against any simplistic assumptions.

5. Conclusions

All the analysed Salcombe ingots are of unalloyed copper with low levels of impurities. Sulphide inclusions are present in all the metallographic sections studied. Analysed ingots have bulk sulphur contents of 0.32–0.79%, but they are much lower (0.03–0.06%) in the artefacts. Although it is not possible to identify the sources of copper ore used for the ingots based merely on the chemical compositions the Salcombe ingots were found to have a quite similar impurity pattern to the Hertford Heath ingots (except for iron) and some similarity to Sardinian ingots, but distinct differences to the Uluburun ingots. The chemical compositions of the Salcombe ingots point to British or Western European sources for the majority of them while connection with somewhere else cannot be excluded for some of them.

It is inconclusive how the Salcombe ingots were made. The very low concentration of iron and the absence of Cu₂O inclusions, on the one hand, suggest that the ingots were produced by the primitive smelting process as primary smelting products rather than products from remelting or refining of primary smelting lumps. The dense metal with very low porosities, on the other hand, suggests the product of refining and re-casting operations in reducing conditions. The small ingots were unlikely resulted from breaking of big ones.

This study provides extensive and direct evidence of the production and maritime movement of large quantities of pure metal ingots – both tin (Wang et al., 2016a) and now copper – across northwest Europe during the Middle-Late Bronze Age (c. 1300–800 BC). The copper ore source or sources that were exploited to produce the Salcombe copper ingots is a major question for further research which will involve lead isotope analysis. This is particularly pertinent due to the compositional variation in the analysed copper ingots identified in this paper. It is also hoped that the chemical analysis of the Salcombe bronze artefacts to be carried out in the future would identify whether the artefacts were made from comparable ingots or those from other copper sources. Recent and detailed research by Williams (2017) indicates that the exploitation of the Great Orme, Wales, which is currently the only copper mine known to have been exploited in Britain during this period, had peaked between c. 1600–1400 BC and was subsequently only exploited at a small-scale. Hence, the exploitation of new copper ore sources needs to be considered for Salcombe, as well as the other sites in Britain where copper ingots have been identified. This resonates at a pan-European scale where it is now widely agreed that the lead isotope and trace element data indicate a major change in the scale of production at a select number of copper ore sources supplying metal over long distances from c. 1600/1500 BC and do not indicate the existence of a large continental pool of compositionally homogenous, recycled metal (Radiivojević et al., 2018). This future research should provide indications not only on the maritime route being taken by the Bronze Age boat or boats wrecked off the coast of Salcombe but also to our understanding of trade across Middle-Late Bronze Age northwest Europe.

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