Journal of Archaeological Science 53 (2015) 492–503

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Copper processing in the oases of northwest Arabia: technology, alloys and provenance

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A R T I C L E I N F O

Article history:
Received 19 December 2013
Received in revised form
21 October 2014
Accepted 25 October 2014
Available online 11 November 2014

Keywords:
Archaeometallurgy
Copper smelting
Arsenical copper
Bronze alloying
Saudi Arabia
Late Bronze Age
Roman
Arabian Peninsula

A B S T R A C T

Very little is known about early metallurgical activity in the north-western part of the Arabian Peninsula, despite the region's cultural importance. To begin to address this research lacuna, metallurgical remains including crucible fragments, metal dross and a copper artefact were sampled from two oases in northwest Arabia, Qurayyah and Tayma. The metallurgical activity in Qurayyah is dated to the Late Bronze Age, and in Tayma to the Roman/Late Roman period. At both sites we identified evidence for copper alloying and refining. Small scale copper smelting might also have been practiced in Qurayyah. Arsenical copper was processed at both sites, but in Tayma tin bronze and leaded tin bronze dominated. The chemical analysis of metal prills in crucible linings showed that fresh copper and tin instead of scrap metal were employed in these processes. Lead isotope analysis indicates that at least some of the Tayma metal was imported. Access to raw materials from remote areas is consistent with the importance of Tayma in the trading network of northwest Arabia.

1. Introduction

The oases of northwest Arabia were important nodal points in the overland caravan routes between south and north Arabia, acting also as markets for the exchange of goods (Macdonald, 1997). The emergence and development of the Arabian incense trade route from around 1000 BC (Finkelstein, 1988; Macdonald, 1997; Byrne, 2003; Jasmin, 2005; Hausleiter, 2012) made this region a crucial junction between the southern Arabian Peninsula and cultures and states in Mesopotamia, the Eastern Mediterranean and the Arabah (Edens, 1992). Besides aromatics, copper is recognised as one of the main goods flowing along this route (Edens and Bawden, 1989; Rothenberg and Glass, 1983; Finkelstein, 1995, 103–126; Tebes, 2007). Despite its importance, copper metallurgy in this area has been rarely studied, and relatively little is known about the origin of the metal and the types of alloys used in northwest Arabia, and more generally about metallurgical processes in oasis settlements.

Since 2004 a joint multidisciplinary research project between the Saudi Commission for Tourism and Antiquities and the German Archaeological Institute sheds new light on these issues. The archaeological findings from two oasis sites, Tayma (Eichmann et al., 2006a, 2010, 2011, 2012; Hausleiter, 2010; Hausleiter, 2011; Hausleiter et al. forthcoming) and Qurayyah (Hanisch-Gräfe et al., 2008), have revealed the first evidence for copper metallurgy in this area. Selected crucible fragments, a metal artefact, slag pieces and metal dross have been analysed in order to reconstruct the metallurgical activities.

1.1. Archaeological background of Qurayyah and Tayma

The site of Qurayyah lies 70 km northwest of Tabuk in northwest Saudi-Arabia (Fig. 1), on the pilgrim and trade route connecting Yemen with the Levant (Parr, 1997). Previous archaeological research at the site was limited to survey activities in 1968 by Parr et al. (1970) and by Ingraham et al. (1981) in 1980. Important findings at this site include multi-chrome Qurayyah Painted Ware (QPW), which was also widely identified across northwest Arabia, Jordan (including the Wadi Arabah) and the Southern Levant (Intilia, forthcoming). It has been dated to the late 2nd millennium

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http://dx.doi.org/10.1016/j.jas.2014.10.030

Fig. 1. Map of northwest Arabia, the Eastern Mediterranean and Mesopotamia, with sites mentioned in the text highlighted.

BC (usually to the 13th/12th century BC). Local production of QPW at Qurayyah and Tayma has now been confirmed by archaeometric analysis (Daszkiewicz, 2014). Significantly, the same type of pottery was identified in the Egyptian mining and smelting site at Timna and a number of sites in the Negev. Timna is located less than 150 km north of Qurayyah, and the Egyptian mining activities there were dated to the nineteenth dynasty (1300–1150 BC), until very recently providing the main basis for the dating of QPW (Rothenberg, 1972, 1988; see however Ben-Yosef et al., 2012). This date has now been confirmed by stratigraphic evidence and ^{14}C-dates at Tayma, although the end of QPW remains a matter of debate (Hausleiter, 2014). According to Avner (2014) mining at Timna may have started earlier than the Egyptian presence. The people then living in Qurayyah might have been involved in the production and circulation of Timna copper (Rothenberg and Glass, 1983; Parr, 1997).

Tayma, located c 300 km south-east of Qurayyah, was a key stop on the incense road and is one of the most important archaeological oasis sites in northwest Arabia (Hausleiter, 2012). Ground water availability is believed to have been one of the main attractions for agricultural residents and caravan travellers (Fachhochschule Lübeck, 2014). The oasis had a wall system more than 18 km in length (Bawden et al., 1980; Schneider, 2010; Hausleiter, 2011, 107 Fig. 4) and its northern part probably protecting arable soils from erosion into the surrounding sabkha (salt flats). Six different occupational periods have been recognised at Tayma (Hausleiter, 2011), with the earliest dated not later than the 4th millennium BC (Engel et al., 2011). The new evidence from the Saudi Arabian–German project suggests that, contrary to previous hypotheses, the occupation of Tayma was continuous. Since the Middle Bronze Age, Tayma was in contact with Syria and the Levant (Al-Hajiri, 2011); from the Late Bronze Age onwards, political and then commercial contacts with many other cultures including Egypt, the Mediterranean, Assyria and Babylonia are attested. The ten-year residence of the Late Babylonian king Nabonidus (556–539 BC) is evidenced by a stele with a Babylonian cuneiform inscription as well as some other fragmentary texts (Eichmann et al., 2006b; Hausleiter, 2011; Schaudig forthcoming). This episode was followed by the rule of the Achaemenids, at Tayma most prominently represented by the 'Tayma Stone' (Stein, 2014), before the Lihyanite Kingdom and then the Nabatean Kingdom took control of the site (Hausleiter, 2012) until its incorporation into the Roman Empire as part of *Provincia Arabia* (Tourtet and Weigel, 2015). During these later periods, the extent of the settlement was much reduced (Edens and Bawden, 1989; Hausleiter, 2011) but substantial architectural remains survived.

2. Samples and research question

The research presented here is a pilot project providing the first analysis of pre-Islamic metallurgical remains from this area, highlighting the potential contribution of these analyses to research concerning metallurgical tradition, metal trade, and other economic activities in this area. It is expected that our research will

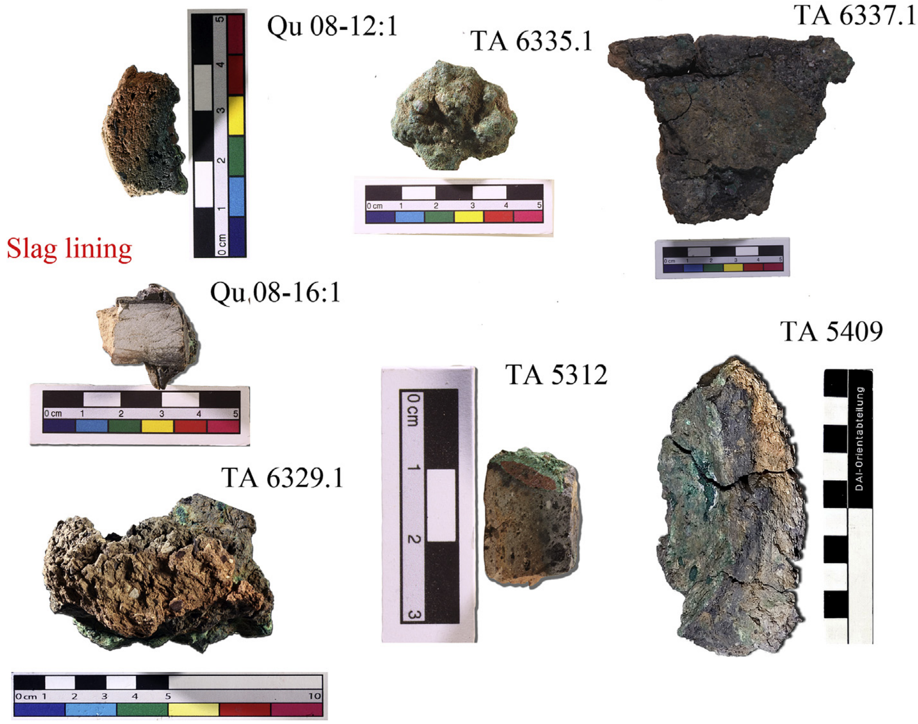

Fig. 2. Photos of some samples from Qurayyah and Tayma. TA 6337.1 and TA 5409 are two large crucible fragments. Qu 08-12:1 and TA 5312 are crucible fragments. Qu 08-16:1 and TA 6329:1 are furnace fragments. TA 6335.1 is metal dross.

stimulate further archaeometallurgical and archaeological research in Arabia.

Three samples from Qurayyah were available for analysis. Qu 08-13:1 is a heavily corroded copper pin collected from the kiln area of Qurayyah. Qu 08-12:1 is a fragment of a crucible, found near "Wall D". Qu 08-16:1 is a piece of burnt stone with a thin layer of slag lining (Fig. 2), collected from the "Graves" area on the rock plateau (Parr et al., 1970; Hanisch-Gräfe et al., 2008). At least sample Qu 08-16:1 can be dated to the Late Bronze Age, based on accompanying pottery finds. The same date is probable also for the other samples from Qurayyah.

The Tayma samples were collected from secondary contexts in the SW part of the central area of ancient occupation (Area D). They were recovered from debris filling an area with installations of a possible workshop (phase D:3a; not necessarily metallurgical and surely with no traces of fire) adjacent to and later than residential buildings (phase D:3b) as well as from the fill of a large cellar or storage unit of the earlier phase. The area is located southwest of an extended residential area dating from the Nabataean to Late Antiquity (Area E-South/F). Though not stratigraphically connected with the former, this horizon of the Area D occupation can be dated to the Roman to Late Roman periods (even though an earlier or later

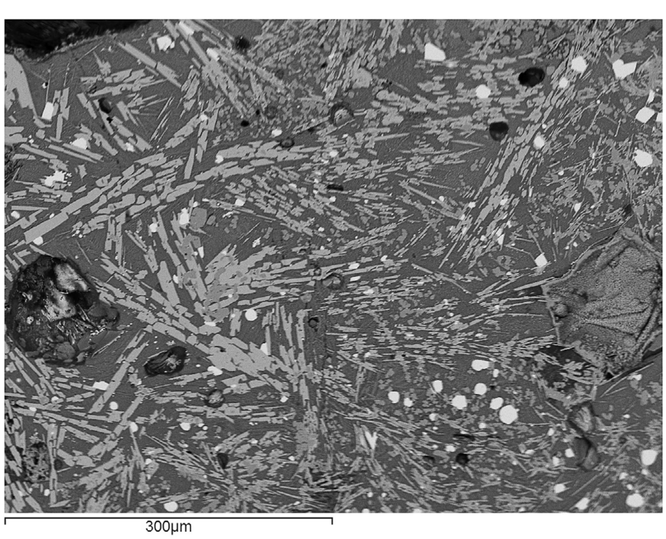

Fig. 3. BSE image of Qu 08-12:1. Plate-to needle-shaped delafossite (light grey) is widely distributed. Bright particles are copper.

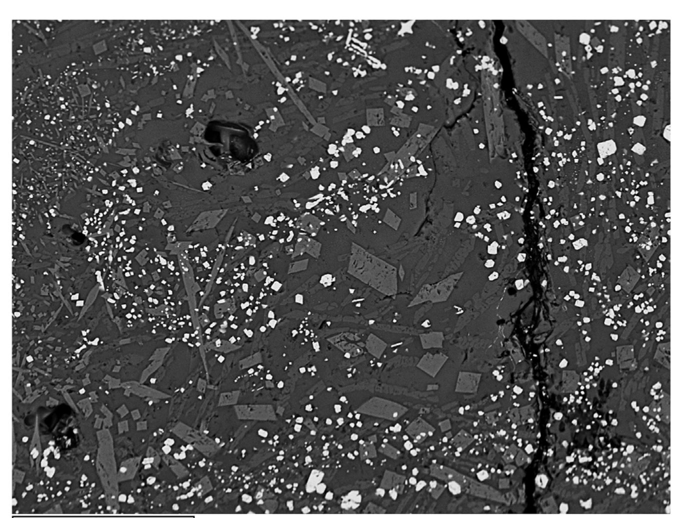

Fig. 4. BSE image of Qu 08-16:1. Medium grey crystals are pyroxenes. Bright grey cubic crystals are magnetite.

date is also possible) by means of general similarity in architecture and occupation sequence as well as preliminary pottery analysis (at maximum 1st century BC to 3rd/4th century AD). The filling, though, may have occurred at a later time (Hausleiter et al. forthcoming). Altogether, 56 metallurgical items were collected from five stratigraphic units of Occupation Level D:3. Six object numbers (TA 5312, TA 5409, TA 5675, TA 6329, TA 6335, TA 6337) have been allocated to the samples, but only in two cases substantial remains of the original crucibles could be identified. TA 5409 is a rim sherd of a rather flat open vessel with pierced holes in its wall. TA 6337.1 is a larger body sherd, probably a base fragment of a crucible. All other fragments are too small to be assigned to a specific part of the body.

Fourteen samples from Tayma including crucible, furnace and metal dross fragments were selected for this study. Their detailed information can be found in Table 1. Three of them were identified as dross, i.e., lumps of heavily burnt metal (Fig. 2: 3); the other eleven are all technical ceramics, most of them lined on their inside with black slag (Fig. 2). The exterior surface of some of the samples is rough and low fired; these samples are probably furnace fragments. Others, with relatively complete and smooth exterior surfaces could be fragments of crucibles. The reddish exterior and partially vitrified and black bloated interior suggest that they were heated from the inside, as is typical for early crucibles (Rehren, 2003; Thornton and Rehren, 2009).

3. Methods

We used micro-chemical analysis and microscopic examination to extract relevant metallurgical information (Rehren, 2003; Rehren and Pernicka, 2008) and lead isotope analysis for the discussion of provenance. The samples were cut to expose areas where abundant metallurgical remains are present. The cross-sections were impregnated with epoxy resin, mounted and polished. Standard procedures were followed to prepare them for optical microscopy (OM) and Scanning Electron Microscopy with Energy-Dispersive Spectrometry (SEM-EDS). Details of all analytical procedures are given in the online Supplementary Material (OSM).

4. Results

4.1. Qurayyah

The copper pin Qu 08-13:1 is completely corroded, with more than 10 wt% oxygen in the SEM-EDS analysis. No alloying elements such as tin, lead or arsenic were detected. In contrast, the two slag samples show significant readings of arsenic, either in their bulk composition or the metal prills trapped in the slag.

The slag attached to the crucible fragment Qu 08-12:1 is very rich in iron, copper and arsenic oxides (Table 2), and contains high amounts of cuprite, delafossite and magnetite (Fig. 3). Magnetite is a common phase in copper smelting slag, while cuprite and delafossite are usually treated as indicators of melting or refining slag, forming under oxidizing conditions (Craddock, 1995, 204; Bachmann, 1982, 16); only in the context of very early metallurgy, they are common also in smelting slag (Radivojević et al., 2010; Müller et al., 2004). Here, we interpret this phenomenon as slag formed during the re-melting of iron-rich arsenical copper, possibly as part of fire-refining primary raw metal (Merkel, 1986; Rehren et al., 2012) (see Table 3).

Table 1
Information and analytical method used for all seventeen samples from Qurayyah and Tayma involved in this study.

Site	Sample code	Context	Description	Chronology	Cut sample	Analytical method
Qurayyah	Qu 08-12:1	Surface near "Wall D"	Crucible fragment	Probably Late Bronze Age (LBA), 13th – 12th century BC	Cross section	SEM-EDS Pb Isotope
	Qu 08-13:1	Surface, Kiln area	Copper pin	Probably LBA	Cross section	SEM-EDS
	Qu 08-16:1	Surface, near Graves on Rock Plateau	Burnt sandstone	Probably LBA	Cross section	SEM-EDS Pb Isotope
Tayma	TA 5312	Fill of Building D-b2:Room 1 (of phase D:3b)	Crucible fragment	Roman to Late Roman (1st to 3rd/4th century AD), but could be earlier	Cross section	SEM-EDS Pb Isotope
	TA 5335	Fill of area with installations (of phase D:3a), SU 2453	Crucible/furnace fragment	Roman to Late Roman or later	Slag lining	SEM-EDS
	TA 5409	Fill of area with installations (of phase D:3a), SU 3927 (beneath SU 2453)	Crucible fragment	Roman to Late Roman or later	Slag lining	Pb Isotope
	TA 5675	Ash lens SU 3942 covering wall SU 3944 (D:3)	Crucible fragment	Roman to Late Roman or later	Cross section with slag lining	SEM-EDS Pb Isotope
	TA 6329.1	Fill of area with installations (of phase D:3a), SU 2453	Ten fragments, from one or more crucibles/furnaces	Roman to Late Roman or later	Slag lining	SEM-EDS Pb Isotope
	TA 6329.9				Slag lining	SEM-EDS
	TA 6335.1	Fill of area with installations (of phase D:3a), SU 3927 (beneath SU 2453)	Ten fragments, from one or more crucibles/furnaces	Roman to Late Roman or later	Metal dross	SEM-EDS Pb Isotope
	TA 6335.3				Cross section	SEM-EDS Pb Isotope
	TA 6335.4				Metal dross	SEM-EDS
	TA 6335.10				Slag piece	SEM-EDS
	TA 6337.1	Fill of area with installations (of phase D:3a), SU 4425 (beneath SU 2453)	Three fragments from one crucible	Roman to Late Roman or later	Slag lining	SEM-EDS Pb Isotope
	TA 6337.5		Ten fragments from one or more crucibles		Metal dross	SEM-EDS Pb Isotope
	TA 6337.10				Cross section with slag lining	SEM-EDS
	TA 6337.11				Cross section with slag lining	SEM-EDS

Table 2
Bulk chemical composition of slag and ceramics from Qurayyah. Data in weight percent, based on SEM-EDS area analyses. Copper, tin, arsenic and lead are excluded from the bulk composition in this table (see notes following the table).

Code	Type	Na_2O^*	MgO^*	$Al_2O_3^*$	SiO_2^*	$P_2O_5^*$	K_2O^*	CaO^*	TiO_2^*	FeO^*	CuO	As_2O_3	SnO_2	PbO
Qu 08-12:1	Slag	0.5	1.8	4.2	28	0.3	1.2	11	bdl	53	26	8.6	bdl	bdl
Qu 08-16:1	Slag	1.2	1.5	8.1	52	0.1	2.8	11	0.3	23	3.9	bdl	bdl	bdl
Qu 08-12:1	Ceramic	0.7	0.8	16	71	bdl	3.3	3.0	0.7	4.6	bdl	bdl	bdl	bdl

*To facilitate comparison between ceramic and crucible slag, the oxides marked with * were recalculated to 100% without the four base metal oxides (CuO, As_2O_3, SnO_2 and PbO). These are presented as found during SEM-EDS analysis. bdl = below detection limit, estimated at around 0.1 wt% for most oxides. Oxygen was calculated according to stoichiometry. Sulphur is below detection limit in all cases.

Sample Qu 08-16:1 consists of a thin coating of slag on a sandstone fragment, most likely from a furnace. Its relatively low concentrations of copper and alloying elements fit well with smelting slag. Significantly, arsenic is not detectable by SEM-EDS in the bulk analysis of this sample, although there are numerous arsenical copper prills in the slag, which indicates a reducing atmosphere. In contrast, despite its relatively low total iron oxide content of ca. 23 wt% FeO (Table 2), the slag is rich in magnetite, sometimes surrounding copper metal prills containing 2 to 6 wt% arsenic (Fig. 5, Table 4). This phenomenon may indicate that iron was burnt out from an initially iron-rich arsenical copper (cf. Rehren et al., 2012), indicating more oxidising conditions just before the slag solidified. It needs to be borne in mind that the slag in this sample is directly attached to a furnace wall fragment, and both the relatively high silica content and the redox condition in this part may not represent the central area of the furnace, where the metallurgical process really happened.

Table 3
Chemical composition of delafossite and magnetite crystals in Fig. 3. Data in weight percent, based on SEM-EDS area analyses. Oxygen data is reported as measured. Ideal composition of delafossite and magnetite as per stoichiometry.

	O	Mg	Al	Ti	Fe	Cu
Delafossite	18	bdl	0.7	0.4	37	44
Delafossite	17	bdl	1.1	0.3	36	46
Delafossite	18	bdl	0.9	0.7	34	46
Ideal delafossite	*21*	-	-	-	*37*	*42*
Magnetite	27	0.3	1.2	0.8	71	bdl
Ideal magnetite	*28*	-	-	-	*72*	–

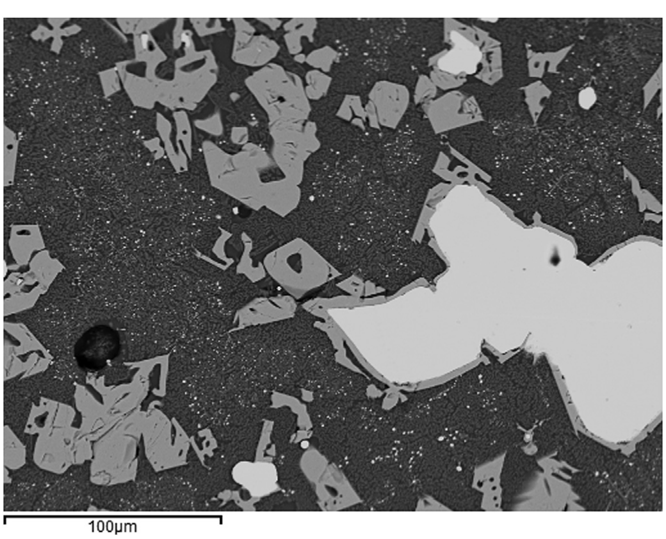

Fig. 5. BSE image of Qu 08-16:1, showing light grey cubic magnetite crystals in a dark grey silicate matrix. Note the magnetite surrounding copper prills rich in arsenic (bright), probably forming from the oxidation of iron metal initially present in the alloy. The big copper prill has 4.7 wt% As (Table 4 No. 4).

In summary, two of the finds from Qurayyah point to a potential smelting operation producing iron-rich arsenical copper in a sandstone-built furnace (sample Qu 08-16:1); this alloy would then have been re-melted in a crucible, thereby burning out most of the iron from it, but also losing some of the copper and arsenic into the crucible slag (sample Qu 08-12:1). Such a sequence of operations has recently been suggested for an Early Bronze Age large-scale smelting site for arsenical copper in central Iran near Arisman (Rehren et al., 2012), and may well have persisted on a small scale into later periods.

4.2. Tayma

The material from Tayma is both more abundant and more diverse than that from Qurayyah. It includes three samples identified as metal dross (TA 6335.1, TA 6335.4 and TA 6337.5). Dross consists primarily of base metal oxides and is characteristic waste of metal melting or casting, formed during high temperature oxidation, which is burning of metal during its processing. All three samples are mainly composed of oxides of copper, tin and lead, with residual metallic copper and lead prills found as islands in the matrix of oxides. The original alloy type of this dross was leaded tin bronze, but the exact composition is hard to estimate due to the different oxidation rates of the various metals involved (Kearns et al., 2010) and possible post-depositional loss of copper.

Bulk chemical compositions of all other samples are given in Table 5. Two crucible samples, TA 5312 and TA 6335.3, do not have real slag lining but just corroded metal particles and metal prills trapped in vitrified ceramics. The corroded metal particle in TA 5312 shows only arsenic as the alloying element, and in TA 6335.3, the corroded metal contains much lead chloride. Almost all slags contain high amounts of copper oxide reaching from 10 wt% to as high as 60 wt%. In many of them tin oxide exceeds 15 wt% in the bulk, while lead was detected in a couple of samples. Tin oxide occurs as elongated to needle-shaped crystals (Fig. 6 and Fig. 7), with the morphology strongly indicating a high temperature forming history (Rademakers et al. forthcoming). Surrounding

Table 4
Chemical composition of metal prills in Qurayyah samples. Data in weight percent, based on SEM-EDS area analyses.

Number	Code	Type	Composition wt%								
			O	Si	Cl	Ca	Fe	Cu	As	Sn	Pb
1	Qu 08-12:1	Metal prill	0.9	bdl	bdl	bdl	bdl	96	3.3	bdl	bdl
2	Qu 08-12:1	Metal prill	1.4	0.4	bdl	0.3	3.5	92	2.2	bdl	bdl
3	Qu 08-12:1	Corroded metal	19	bdl	8.0	0.7	0.6	70	2.2	bdl	bdl
4	Qu 08-16:1	Metal prill	0.7	bdl	bdl	bdl	bdl	95	4.7	bdl	bdl
5	Qu 08-16:1	Metal prill	0.7	bdl	bdl	bdl	2.5	91	5.7	bdl	bdl
6	Qu 08-16:1	Metal prill	0.6	bdl	bdl	bdl	2.1	92	5.2	bdl	bdl
7	Qu 08-16:1	Metal prill	bdl	bdl	bdl	bdl	2.4	94	3.2	bdl	bdl

* bdl means below detection limit. All elements as analysed, incl. oxygen.

Table 5
Bulk chemical composition of slag and crucible samples from Tayma. Data in weight percent, based on SEM-EDS area analyses. Copper, tin, arsenic and lead are excluded from the bulk composition in this table (see notes following the table).

Code	Type	Composition wt%													
		Na_2O^*	MgO^*	$Al_2O_3^*$	SiO_2^*	$P_2O_5^*$	SO_3^*	K_2O^*	CaO^*	TiO_2^*	MnO_2^*	FeO^*	CuO	As_2O_3	SnO_2	PbO
TA 5335	Slag	bdl	4.5	10	32	0.8	bdl	2.4	19	bdl	bdl	32	15	bdl	17	bdl
TA 5675	Slag	bdl	6.2	10	29	0.5	3.8	0.5	30	bdl	bdl	20	59	3.6	bdl	bdl
TA 6329.1	Slag	bdl	8.3	10	34	2.8	bdl	0.9	31	0.3	bdl	13	25	bdl	19.8	bdl
TA 6329.9	Slag	0.9	5.0	11	38	1.3	bdl	2.5	34	0.4	0.3	6.3	17	bdl	4.3	bdl
TA 6335.10	Slag	bdl	4.2	12	39	1.3	0.4	0.9	35	0.7	0.4	6.5	8.6	bdl	5.5	6.3
TA 6337.1	Slag	bdl	5.3	11	59	bdl	bdl	bdl	21	bdl	bdl	3.7	7.8	bdl	11	bdl
TA 6337.10	Slag	1.2	4.9	14	38	1.4	bdl	2.0	30	0.3	bdl	8.0	50	bdl	14	bdl
TA 6337.11	Slag	1.8	3.9	13	35	0.3	bdl	0.9	18	0.7	bdl	26	16	bdl	15	bdl
TA 5335	Ceramic(v)	0.7	0.9	26	58	bdl	bdl	5.1	0.7	1.4	bdl	7.4	1.9	bdl	1.3	bdl
TA 6329.1	Ceramic(v)	bdl	0.8	22	68	bdl	bdl	4.3	0.5	0.9	bdl	3.0	2.5	bdl	bdl	bdl
TA 6337.1	Ceramic(v)	0.5	1.1	24	60	bdl	bdl	6.1	1.5	1.2	bdl	6.0	5.6	bdl	bdl	bdl
TA 5312	Ceramic	0.3	1.4	25	59	bdl	bdl	4.6	0.6	1.2	bdl	7.8	0.8	bdl	bdl	bdl
TA 5675	Ceramic	0.6	0.9	23	59	bdl	bdl	4.8	0.6	1.3	bdl	9.6	bdl	bdl	bdl	bdl
TA 6335.3	Ceramic	0.3	0.8	24	63	bdl	bdl	4.7	0.5	1.2	bdl	5.8	bdl	bdl	bdl	bdl
TA 6337.10	Ceramic	0.6	0.9	24	61	bdl	bdl	4.3	0.2	1.2	bdl	7.8	bdl	bdl	bdl	bdl
TA 6337.11	Ceramic	0.8	0.8	24	62	bdl	bdl	4.8	0.1	1.2	bdl	6.3	bdl	bdl	bdl	bdl

*All results for slag, bulk ceramic and sandstone were obtained through area analysis (1.2 mm × 0.9 mm) by SEM-EDS. To facilitate comparison between ceramic and crucible slag, the oxides marked with * were recalculated to 100% without the four base metal oxides (CuO, As_2O_3, SnO_2 and PbO). These are presented as found during SEM-EDS analysis.
* (v) means vitrified ceramic. bdl means below detection limit.
Some samples, such as TA 5312, do not have a real slag lining but only vitrified ceramic with copper prills and copper corrosions.

these tin oxides, crystals of tin–calcium oxide (malayaite) can often be identified. Most likely, tin metal was first oxidised to tin oxide crystals and then reacted with the calcium-rich slag matrix. Tin-rich spinels were also identified in many samples, and magnetite is abundant in most samples.

The metal prills in most Tayma samples are bronze and leaded bronze (Table 6). Some of these prills have very high tin contents (>24 wt%) and show tin-rich δ and ε phases in their metallographic structure (Fig. 9). These are very rarely encountered in normal tin bronzes and are highly unlikely to represent the final products; instead they are probably intermediate products of the processes carried out in these crucibles (see below). Sample TA 5675 has several tin bronze prills even though its bulk analysis showed no tin (Table 4). Only one sample is tin-free (TA 5312); it has no slag matrix but arsenical copper prills trapped in vitrified ceramic (Fig. 8).

Many bronze prills also contain several percent arsenic, probably as an impurity from the copper, and some of these prills have arsenic-rich inclusions (>20 wt%) (Fig. 10). The iron concentration of metal prills from Tayma is systematically lower than in the Qurayyah prills (mainly bdl to 1 wt% and only in TA 5675 exceeding 2 wt%).

Overall, with the exception of TA 5312, the Tayma samples are all consistent with the production and processing of tin bronze or leaded tin bronze. Several of the crucible samples show rather oxidising conditions, as indicated by the prevalence of metal oxides; these samples link directly to the dross lumps, which are likely to have formed under the same oxidising conditions. They may represent intentional fire refining of bronze scrap, or unintentional metal loss during remelting bronze under less controlled redox conditions. Those prills which only consist of high-tin phases

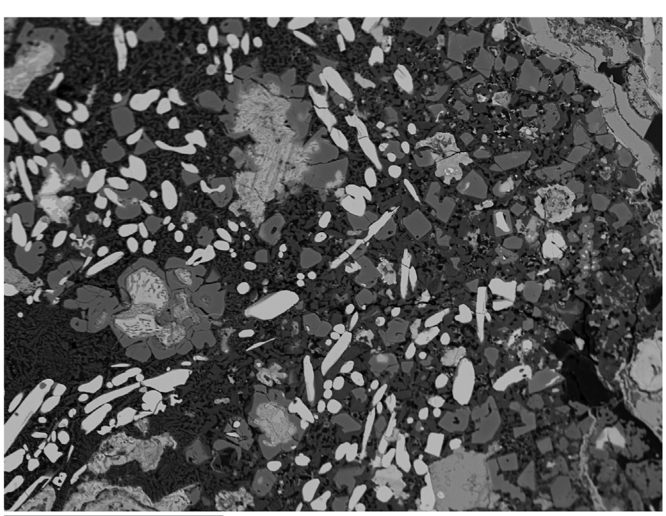

Fig. 6. BSE image of slag sample TA 5335, showing a cluster of tin oxide (bright elongated crystals) and magnetite (medium grey cubic crystals), often with a core of tin spinel (light grey). See Table 4 for bulk composition of this slag.

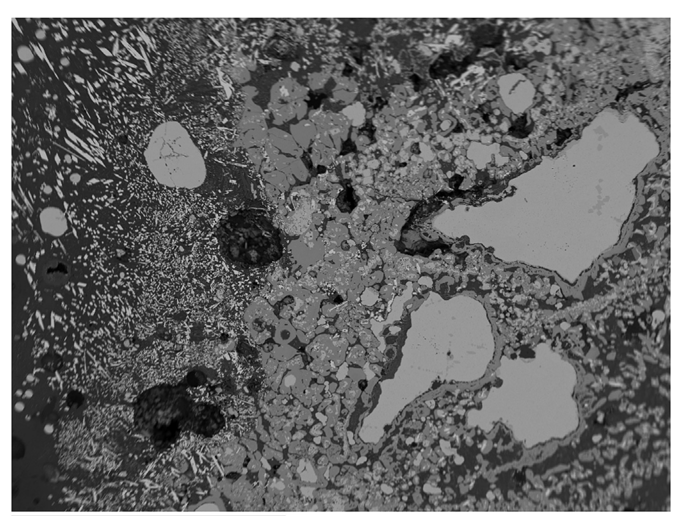

Fig. 7. BSE image of slag sample TA 6337.1, showing tin oxide needles (bright, left), surrounded by malayaite (Sn–Ca oxide, light grey, centre). The large bright particles are copper metal, surrounded by copper oxide. See Table 4 for bulk composition of this slag.

Table 6
Chemical composition of metal prills and corroded metal particles in Tayma samples. Data in wt%, all elements including oxygen as determined by SEM-EDS small area analysis.

Number	Code	Composition wt%						
		O	Fe	Cu	Ni	As	Sn	Pb
1	TA 5312	2.7	1.0	74	bdl	22	bdl	bdl
2	TA 5312	1.1	0.8	68	bdl	30	bdl	bdl
3	TA 5312	1.1	0.5	92	bdl	6.4	bdl	bdl
4	TA 5312	1.2	0.5	91	bdl	7.3	bdl	bdl
5	TA 5312	0.9	0.4	93	bdl	5.4	bdl	bdl
6	TA 5312	0.7	0.5	95	bdl	3.4	bdl	bdl
7	TA 5312	2.4	0.3	91	bdl	6.8	bdl	bdl
8	TA 5335	2.0	bdl	44	bdl	bdl	54	bdl
9	TA 5675	1.6	6.4	83	bdl	1.9	7.6	bdl
10	TA 5675	0.8	2.4	90	bdl	5.7	1.1	bdl
11	TA 5675	0.9	3.8	91	bdl	2.8	1.8	bdl
12	TA 5675	bdl	3.5	81	1.5	1.0	13	bdl
13	TA 6329.9	bdl	0.8	96	bdl	bdl	3.4	bdl
14	TA 6329.9	bdl	bdl	98	bdl	bdl	2.5	bdl
15	TA 6335.3	15	bdl	53	bdl	bdl	7.5	25
16	TA 6335.10	bdl	bdl	96	bdl	bdl	bdl	3.6
17	TA 6335.10	bdl	bdl	72	bdl	0.2	25	2.7
18	TA 6337.1	2.0	bdl	92	bdl	bdl	5.8	bdl
19	TA 6337.1	bdl	bdl	76	bdl	bdl	24	bdl
20	TA 6337.1	3.4	bdl	53	bdl	3.8	40	bdl
21	TA 6337.1	1.3	bdl	67	bdl	2.8	29	bdl
22	TA 6337.10	0.6	bdl	97	bdl	bdl	2.5	bdl
23	TA 6337.11	2.3	bdl	90	bdl	bdl	7.5	bdl
24	TA 6337.11	0.9	bdl	86	bdl	1.1	12	bdl

* bdl means below detection limit. Grey shade1s indicate high tin prills (more than 20 wt% Sn).

(δ, ε and η) are interpreted to indicate the active alloying of tin and copper to produce bronze; either or both of these metals may have contained a significant amount of arsenic and iron as well. Sample TA 5312 is intriguing as it provides evidence for the processing of arsenical copper; at this stage of our research it is impossible to say whether this happened in parallel to the dominant bronze use, or whether the metal melted here was part of the feeder stock for the bronze production. More importantly, the composition of the fill of Room 1 of Building D-b2 included remarkable quantities of Late Bronze to Late Iron Age pottery (Hausleiter et al. forthcoming), which may, however, indicate that TA 5312 is chronologically different from, i.e. earlier than the other samples.

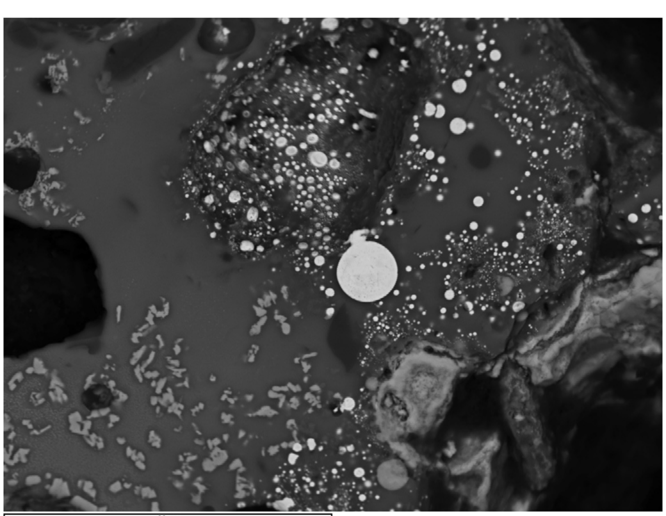

Fig. 8. Arsenical copper prills trapped in the vitrified ceramic of TA 5312. The largest prill's composition is shown in Table 6:4.

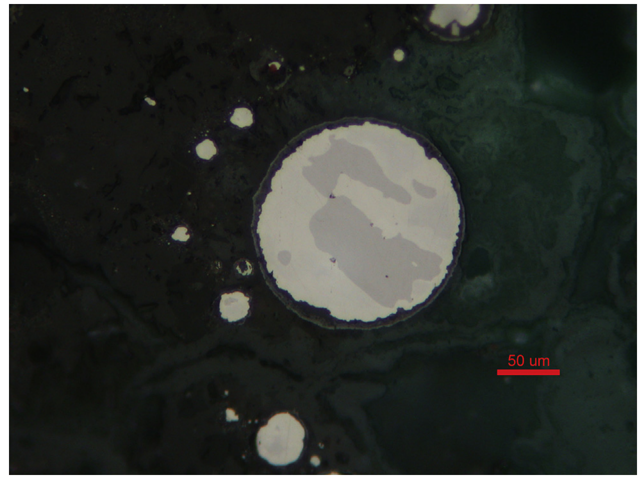

Fig. 9. Optical micrograph of TA 5335. The bronze prill in the centre contains on average 54 wt% tin (Table 5:9). There are two high tin phases (ε and η) identified in this prill. The η phase (light grey) contains 3.2 wt% Fe, 1.4 wt% Co, 35.8 wt% Cu and 59.6 wt% Sn. The ε phase (grey) contains 61.6 wt% Cu and 38.4 wt% Sn.

There is no indication that metal smelting took place at Tayma; the crucible slag composition is fully in line with melting slag formed from the reaction between fuel ash (as indicated by the very high lime, magnesia and phosphate content in the slag compared to the underlying ceramic, Table 4), crucible material (silica and alumina), and some burnt-out metal charge (copper, tin and iron). The increased iron content in some of the crucible slag suggests that the metal worked here was primary iron-containing raw copper and/or tin rather than circulating bronze alloy or scrap, and therefore further supports the argument for local alloying.

5. Lead isotope analysis

In order to gain more insight into the possible origin of the ore and metal used in the two sites, lead isotope abundance ratios were analysed for 10 samples (for analytical procedures see Niederschlag et al., 2003 and OSM), eight from Tayma and two from Qurayyah. There is a clear correlation between archaeological context and lead

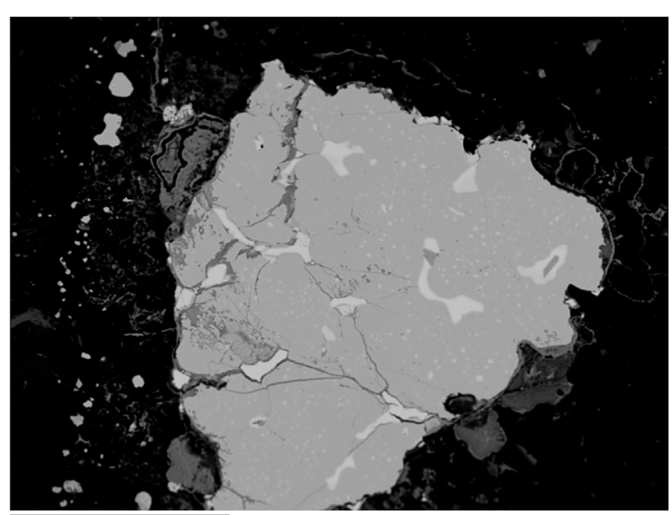

Fig. 10. BSE image of TA 6337.1. The bright phases in the bronze prill are rich in tin and arsenic. The dark inclusions are Co–As phases.

Table 7
Lead isotope abundance ratios of Tayma and Qurayyah samples.

Code	Lab code	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Qu 08-12:1 crucible slag	MA-104274	0.88247	2.1208	17.555
Qu 08-16:1 furnace slag	MA-104275	0.85415	2.0931	18.237
TA 5312	MA-104266	0.83427	2.0710	18.793
TA 5409	MA-104267	0.83597	2.0715	18.754
TA 5675	MA-104268	0.86929	2.1071	17.888
TA 6329.1	MA-104269	0.83499	2.0671	18.753
TA 6335.1	MA-104270	0.83287	2.0639	18.829
TA 6335.3	MA-104271	0.83253	2.0627	18.819
TA 6337.1	MA-104272	0.83644	2.0704	18.719
TA 6337.5	MA-104273	0.83222	2.0616	18.841

isotope composition (Table 7 and Fig. 11). The Tayma and Qurayyah samples form two different clusters in the binary graphs of $^{208}Pb/^{206}Pb$–$^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$–$^{207}Pb/^{206}Pb$. Seven of the eight Tayma samples form a more radiogenic cluster (low $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ values), within which two sub-groups can be identified. It should be noted that the source of lead is not necessarily equal to the source of copper because alloying elements such as tin, arsenic and especially lead itself will contribute their isotopic signature to the final result. It is interesting to find that the three samples which form the lower sub-group (TA 6335.1, TA 6335.3 and TA 6337.5) are all particularly rich in lead. Two of them are metal dross and the other one has corroded metal rich in lead chloride. One sample in the upper sub-group (TA 6329.1) is separated from the other three by its low $^{208}Pb/^{206}Pb$ ratio. This sample is also very rich in tin (nearly as much as copper), but low in lead (bdl in SEM-EDS analysis). It may be argued for these four samples that their lead isotope results are significantly affected by alloying elements and reflect not only the isotopic signature of the copper.

The two Qurayyah samples (Qu 08-12:1 and Qu 08-16:1) and one Tayma sample (TA 5675) have much higher abundance ratios, stretched out over a relatively wide range (Fig. 11). The two Qurayyah samples form the extreme ends of this range, while sample TA 5675 falls in between the two. This sample differs from other Tayma samples by its high content of arsenic (average 3 wt%), iron (av. 4 wt%) and relatively low tin (av. 5.5 wt%) in the metal prills (see Table 6). It is also the only sample to have a few percent each of arsenic and sulphur in the bulk area analyses of the slag (Table 5).

Due to the lack of robust background data from ore bodies and artefacts in this region, the discussion will only suggest potential

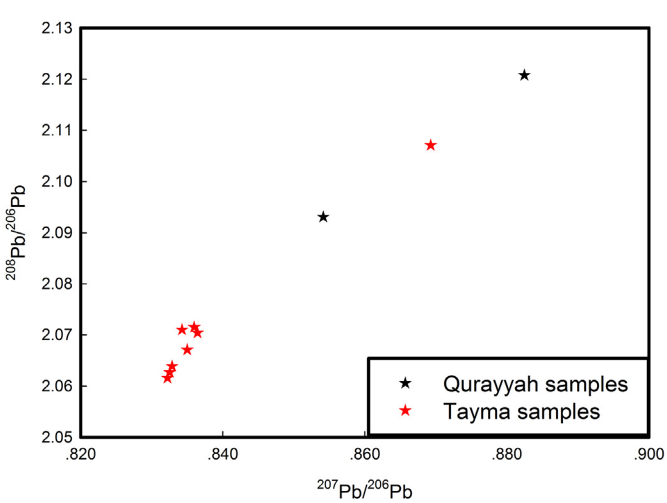

Fig. 11. Binary plot of $^{208}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$ for all Tayma and Qurayyah samples. The samples form two subgroups; both Qurayyah samples are in the sub-group with higher abundance ratios while the majority of Tayma samples are in the more radiogenic group (lower left).

metal sources. Weeks et al. (2009) suggested three main copper sources within and around Arabia which were exploited since before the Iron Age. Geographically, the most likely copper source for Tayma and Qurayyah would be the Jordan rift valley of northwest Arabia with the famous ancient mining and smelting sites at Feinan and Timna (Rothenberg, 1972; Hauptmann, 2007; Weisgerber, 2006). The second major potential copper source for these two sites is in current Oman and the northern United Arab Emirates where copper was exploited as early as the second half of the third millennium BC and at least until the pre-Islamic period (Weeks, 2003). The third potential copper source (Weeks et al., 2009) is the so-called Arabian Shield in southwest Arabia and northeast Africa, split by the Red Sea. Lead isotope data for ores and artefacts from this region match best with Bronze Age artefacts from al-Midamman on the Red Sea coast of Yemen (Weeks et al., 2009: 593–4). Finally, fieldwork in the Sinai Peninsula identified another possible copper source of potential relevance for northwest Arabia (Abdel-Motelib et al., 2012), which may have been exploited already during the Early Bronze Age (Rehren and Pernicka, 2013).

Lead isotopic data from all pre-mentioned ore sources are plotted in Fig. 12. Interestingly, the two Qurayyah samples have little isotopic overlap with published copper ore data from Feinan/Timna. Qu 08-16:1 falls in the middle of several Omani and Sinai ore samples. Due to the complicated nature of lead isotope data from this area, the geological provenance of copper in this sample is hard to be determined. Qu 08-12:1 generally falls in the range of Arabian shield samples and is clearly separated from other sources. However, since not much archaeometallurgical work was carried out in the southwest Arabia and background data used here is whole rock and galena rather than real copper ores, this connection between southwest and northwest Arabia remains to be tested.

Most of the Tayma samples plot in the more radiogenic region and have no good overlap with published data of ore fields surrounding this region. One Tayma sample, TA 5675, locates in the higher abundance ratios regions, and roughly falls in the range of Arabian shield samples.

If we look beyond this regional range, there may be an interesting possibility of relating some Tayma samples to Mediterranean copper and lead sources. The majority of Tayma samples have a reasonably good match with Cypriot copper ores from Limassol, especially with Limassol new data (Stos-Gale et al., 1998) extending the area of Limassol ores to the more radiogenic end (Fig. 13). However, all Limassol samples have slightly lower $^{206}Pb/^{204}Pb$ ratio than the Tayma samples. More caution is indicated if we regard the arsenic concentrations of oxhide ingots from Uluburun as characteristic for copper from Cyprus (Hauptmann et al., 2002); they only have arsenic contents between 0.09 and 0.23 wt% (interdecile range). The very high concentration of arsenic in the Tayma samples then speaks against a connection between Tayma and Cyprus. However, Stos-Gale et al. (1997) have noticed that ores from Limassol forest have quite high arsenic content and could potentially be the raw materials for arsenical copper production. For a more detailed discussion, more precise trace element data would be required. The lower sub-group of three lead-rich samples (TA 6335.1, TA 6335.3 and TA 6337.5) has an isotopic fingerprint close to lead/copper ores from Lavrion in Greece, but their lead isotope abundance ratio most likely indicates the source of lead alloyed to the bronze rather than the source of copper. Copper of these three samples could therefore be either from Lavrion or contaminated with added lead from Lavrion. Significantly, copper ores from Lavrion also have quite high arsenic content (Gale et al., 2009). It is hoped that future trace element analysis of actual bronze artefacts from Tayma, rather than the processing waste, will enable us to distinguish between these copper sources.

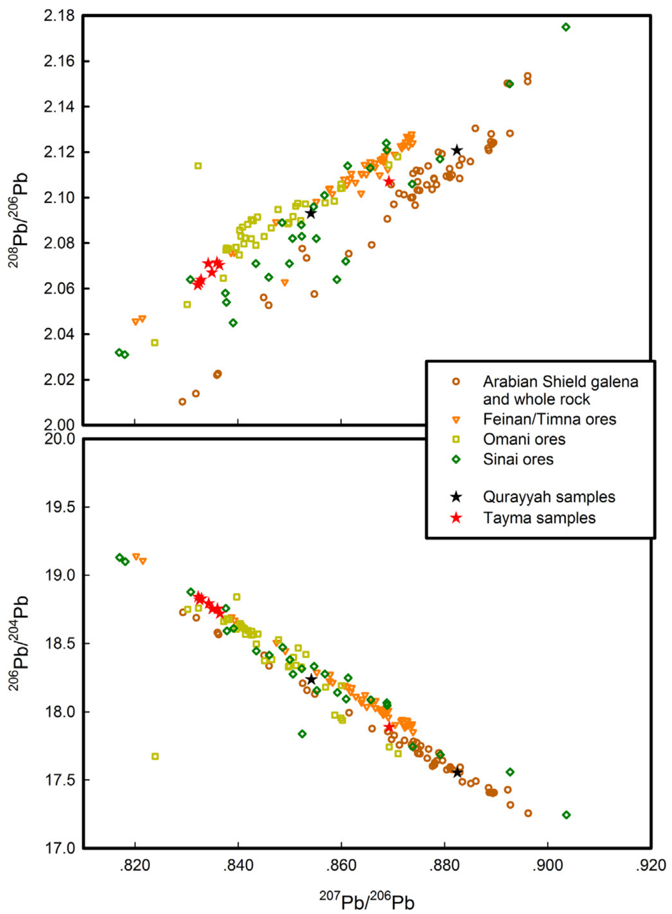

Fig. 12. Comparison of lead isotope results of Qurayyah and Tayma samples with ores from Feinan/Timna, the Sinai, Oman, and Arabian shield galena and whole rocks. Data for Feinan/Timna copper are from Hauptmann et al., 1992, Hauptmann 2007, Gale et al., 1990; Oman ore data from Begemann et al., 2010; Arabian shield galena is from Stacey et al., 1980; Arabian shield whole rock data from Ellam et al., 1990.

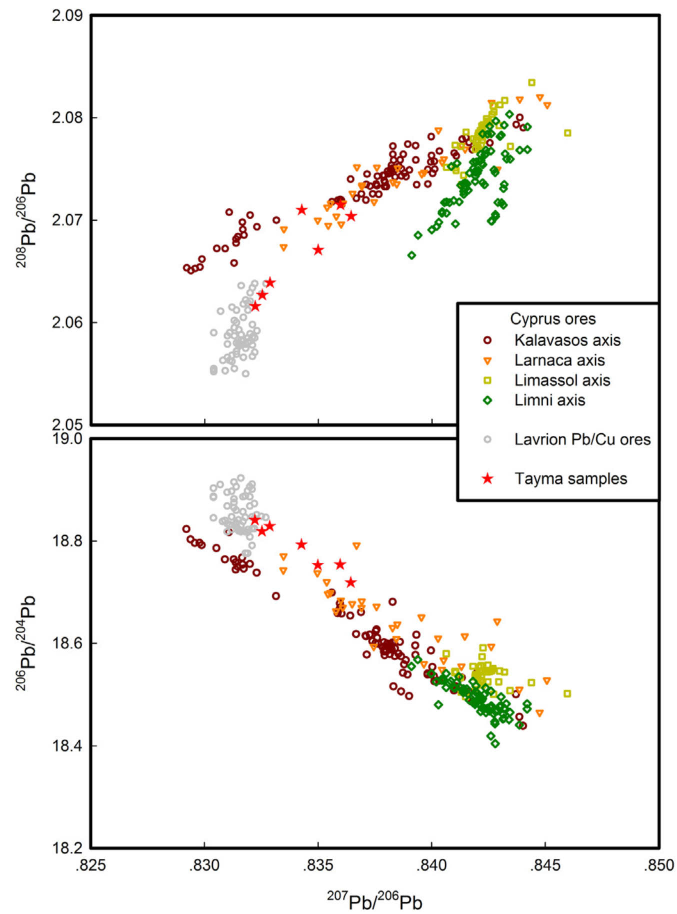

Fig. 13. Comparison of lead isotope results of Qurayyah and Tayma samples with ores from Cyprus and Lavrion. Data from Stos-Gale et al., 1996, 1997 and 1998.

6. Discussion

6.1. *Nature of metallurgy*

6.1.1. *Qurayyah*

The two samples from Qurayyah are consistent with the smelting and remelting/refining of arsenical copper, probably involving sandstone-built furnaces for smelting and ceramic crucibles for refining and casting. So far, no other alloying elements were detected in the crucible fragment (Qu 08-12:1), furnace wall fragment (Qu 08-16:1) and corroded artefact (Qu 08-13:1). The crucible Qu 08-12:1 was formed with non-refractory ceramic with low lime, intermediate iron oxide and high silica content. The high silica content in Qu 08-12:1 can be explained by the large quantity of quartz temper in its fabric. The charge processed in the crucibles most likely was raw copper, fuel such as charcoal, and possibly fluxes. During the process, these would react to form a crucible slag comprising of vitrified ceramic material, fuel ash, and parts of the metal charge, either oxidised or as mechanically trapped prills (Bachmann, 1982, 9–10). Of the various compounds in the slag, alumina is likely to originate only from the ceramic; all other major or minor oxides can come from various sources. To estimate the relative amount of each contributing component in the slag it is therefore sensible to compare the ratios of each oxide to alumina, in order to see whether and how much they are enriched compared to the original ceramic composition. The excessively high FeO/Al_2O_3 ratio in the Qu 08-12:1 slag lining might indicate intentional refining as an important part of metallurgical activities in this site (Table 8).

The sources of the additional iron and silica are likely to be the raw metals and fluxes. The prill analyses have shown that raw copper and copper alloys from these sites contain up to several percent iron; but other alloying agents such as, for example raw arsenic-rich speiss might also introduce some iron into the system. As the high SiO_2/Al_2O_3 ratio shows, silica rich sand may have been added to facilitate the mechanical separation between molten metal and iron oxides by fluxing iron oxides to form slag (Craddock, 1995, 203). The general influence of fuel ash on the lime content has been shown in several other studies (Craddock and Meeks, 1987; Crew, 2000; Müller et al., 2004; Wood, 2009), and is evident also here. The output of this process should be arsenical copper with 2–3 wt% arsenic and only minor amounts of iron, as well as an iron-enriched crucible slag. Overall, the metallurgical evidence from Qurayyah is consistent with the Bronze Age date of the finds. Little

Table 8
Compound ratios for slag and ceramic in Qu 08-12:1.

Type	Ratios of oxides		
	SiO_2/Al_2O_3	CaO/Al_2O_3	FeO/Al_2O_3
Slag	6.6	2.5	12.8
Ceramic	4.3	0.2	0.3

can be said about their origin, except that the one analysed sample (Qu 08-12:1) has lead isotope ratios consistent with Arabian shield whole rock and galena.

6.1.2. Tayma

Tayma crucibles were made with normal clay but lack the rich quartz temper found in the Qurayyah crucible. The main evidence from Tayma points to the melting and alloying of copper and tin in crucibles to produce bronze. Some of these appear to have been used to process fresh iron-rich copper, leading to increased iron oxide content in the crucible slag. The presence of frequent prills of high-tin copper–tin phases strongly indicates the alloying of tin metal or cassiterite with copper to make fresh bronze, as opposed to the simple remelting of existing bronze scrap. Arsenic was also detected in many of these samples, especially in the metal prills. However, as the presence of tin and lead in these prills indicates, arsenic should here be seen as a contamination rather than a major alloying component. The only exception is TA 5312 which contains high-arsenic copper prills (>20 wt% As) but no tin. In this case, arsenical copper might have been the intended product. The slagless nature of this crucible may suggest it was only used to melt rather than refining/alloying arsenical copper.

The lead isotope signatures point to a mixture of metals from different sources, possibly as far as Cyprus and Lavrion, even though we are unable at present to suggest a particular source due to the relative small number of samples and overlapping signatures from potential sources.

6.2. Archaeological impact of this research

The crucial information revealed by the metallurgical reconstruction is that raw metals rather than previously alloyed clean arsenical copper or bronze were used and probably even produced in both sites. Thus, their metallurgical activities were more complex than the simple melting and casting of pre-existing copper alloys. The presence of arsenic in these samples deserves more attention. There have been discussions about the identification of intentional alloying of arsenical copper as opposed to the mere processing of naturally arsenic-rich copper ore (Craddock, 1976; Lechtman, 1991; Tylecote, 1991), and the arsenic content in many Qurayyah metal prills is higher than the levels set by these authors as upper limits for naturally occurring arsenic content. The high arsenic content in Qurayyah samples combined with the fact that no tin bronze has so far been identified at the site may suggest that arsenical copper was intentionally produced at Qurayyah. The lead isotope and chemical analyses for the Qurayyah samples indicate that their copper did not come from Feinan or Timna. It had been suggested earlier that people using Qurayyah Painted Pottery have been working in Timna (Rothenberg and Glass, 1983), and might have brought copper back to Qurayyah. The nature of this relationship between Qurayyah and Timna will now have to be re-considered, as it is possible that arsenic-rich copper sources within the Arabian Peninsula provided the material processed at Qurayyah. This picture of rather autonomous Late Bronze Age oases matches the observation of a local production of Qurayyah Painted Ware at Qurayyah and at Tayma (Hausleiter, 2014; Daszkiewicz, 2014), in addition to the apparent long distance relations of Northwest Arabian oases already during the Middle Bronze Age.

In much of the Old World, arsenical copper became rare in artefacts from the Iron Age and later periods. The arsenic-rich materials (>2 wt% As in many prills) from Tayma then certainly need more attention, especially when most of these samples have lead isotope ratios matching Mediterranean metal sources (Cyprus and Lavrion). Weeks (2003, 85–88) reviewed 154 Iron Age copper-based objects from southeast Arabia and found that their arsenic concentration was considerably lower compared to previous periods. Only three of these objects reached a concentration of 1.0–1.5 wt% As. Craddock (1988) analysed 539 copper objects from Timna and adjacent areas. The mean arsenic content of these is 0.125 wt%, and only four of them contain more than 1 wt% As. Analysis of artefacts from the Jordan valley (Philip et al., 2003) also revealed that arsenical copper was quite rare during the Iron Age. Similarly, analyses of bronzes from Luristan in western-central Iran showed that by the Iron Age arsenic had mostly disappeared from copper-based artefacts, with a mean arsenic content of only 0.3 wt% (Fleming et al., 2005). Arsenical copper was also rarely used in Egypt after the New Kingdom period (16th–11th century BC) (Ogden, 2000, 152–153). For a later period, Ponting and Segal (1998) and Ponting (2002) published the chemical composition of 137 Roman copper-based artefacts from first century Israel and Palestine, and showed arsenic content never exceeding 0.5 wt% and mainly below 0.1 wt%. Also artefacts from the first century AD site of Ed-Dur in UAE generally contain less than 0.5 wt% As (Weeks, 2004). However, there is also some evidence that arsenical copper was used continually in the Iron Age, for example in Tepe Yahya in Iran (Thornton et al., 2002) and Ikiztepe in Anatolia (Özbal et al., 2002). These finds are still relatively old compared to the Late Roman materials from Tayma, and many of these finds are small non-elite artefacts. As Thornton et al. (2002) pointed out, in a socio-economically relatively inactive region, the old traditions of metal production could be preserved for quite a long period even after the introduction of new metals and alloys. Due to the lack of background data and analyses of artefacts, it is still unclear whether a similar theory can be used to explain the persistence of arsenical copper in the late Roman context of northwest Arabia.

According to our reconstruction, metallic tin was used in this site for alloying with copper. Most geological deposits of tin ores are geographically far from northwest Arabia. Although tin deposits also exist in the Eastern Desert of Egypt (Rapp et al., 1999; Muhly, 1993) and central Saudi Arabia (Du Bray et al., 1988), there is no clear evidence that these ores were exploited in ancient times (Weeks, 2003, 167). The extraordinary tin-rich slags found in the first millennium BC site Hajar Ar-Rayhani in Yemen (Fleming and Pigott, 1987) deserve some attention as they may indicate a local tin source in SW Arabia. But in any case, the tin of Tayma would have been imported through trade. Apart from possible copper sources within the Arabian Peninsula, lead isotope analyses of Tayma samples also indicate the possibility of metals coming from the Mediterranean. The setting of Tayma as a major node in the overland trade routes, and the date of the finds to a time when Tayma was in close contact with the Roman Empire are consistent with a scenario where fresh tin, lead and copper might have been imported and worked locally into bronze to serve the local needs.

7. Conclusions

This study of copper processing remains from the oases Qurayyah and Tayma identified the nature of probable metallurgical activities at these two sites as smelting (Qurayyah), alloying and refining (Qurayyah and Tayma). Crucibles used in both sites are made from ordinary clay, and only the Qurayyah crucible was heavily tempered with quartz, improving its suitability for high-temperature use. Arsenical copper was used at both sites, and was the main product in Qurayyah. The source of the Qurayyah copper may be partly linked to deposits in the Arabian Shield. It is likely that arsenical copper was locally produced during the Bronze Age. However, more analyses of artefacts and production remains from Bronze Age Central Arabia are necessary to develop our arguments further.

Tin and leaded tin bronze dominate among the Tayma samples. Tin and lead were both added to copper, probably as metals rather than introduced through bronze scrap; however, arsenic is still a significant minor component of many of the Tayma metal prills. In the Roman period, metallic copper, tin and lead in Tayma were acquired through long distance trade, possibly as far as from the Mediterranean, which indicates the ongoing important status of this site in the trading network of northwest Arabia.

Acknowledgements

Our thanks go to the Saudi Commission for Tourism and Antiquities (SCTA) for the permission to carry out surface survey at Qurayyah in 2008 and 2009 as well as for allowing the export of the samples used in this research. Fieldwork in Qurayyah was funded by the German Archaeological Institute (DAI, Research Clusters 2 and 3); research at Tayma is funded by the German Research Foundation. We would like to thank Mr. Simon Groom and Mr. Kevin Reeves of the Wolfson Archaeological Science Laboratories at the UCL Institute of Archaeology for their kind help in sample preparation and analysis. Our thanks also go to the Institute for Archaeo-Metallurgical Studies (IAMS) for their financial support of this project as part of the first author's MSc research at the UCL Institute of Archaeology. The completion of this paper was made possible by grant NPRP 6-813-6-016 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors. We appreciate the comments and suggestions given by six anonymous reviewers of this paper. Special thanks go to Professor Lloyd Weeks and Dr. Christopher Thornton for their advice on our interpretation of chemical and lead isotope data. Dr. Andrea Intilia (DAI) read the paper and added useful comments. All remaining errors and shortcomings are our own responsibility.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2014.10.030.

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