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Analysis of archaeometallurgical residues from Dymock

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Dr T.P. Young

Abstract

A collection of technical ceramics from context (119) notably included fragments of large cupels. These vessels showed evidence for multiple phases of use and relining. The dross they contained was lead rich and indicated the residues from a small scale oxidative cupellation process for extracting silver from mixed metals, probably recycled scrap.

Other components of the assemblage were extremely small fragments from crucibles and moulds.

The assemblage shows parallels with the fabrication of silver-coated brooches elsewhere in Dymock.

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Methods

This report details analysis of residues from Kyrleside, Dymock, Gloucestershire. The assemblage of archaeometallurgical residues was assessed (Young & Kearns 2010) and found to comprise evidence for a range of activities including iron smelting, iron smithing, the casting of copper-alloy artefacts and the small-scale extraction of silver from base metals. It is the evidence for the latter process, small scale cupellation that has been investigated analytically in the component of the project described in this report, as recommended by the assessment report.

This report details analytical investigations undertaken with a handheld portable X-Ray Fluorescence instrument. Analysis employed a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University, and the National Museum Wales). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 100s. The instrument was controlled by a PC running Bruker's *S1PXRF* software. Data were exported as text files for further imaging and processing in Bruker's *Artax* software. Data are presented here as the net peak area for the principal peaks as reported by *Artax* (Table 1).

A very crude semi-quantitative calibration of the data acquired was performed using a technique (Young 2015) employing a simple linear regression of data presented by Nicholas & Manti (2014) who analysed copper alloy standards using the same instrument and with the same operating conditions as for the present work. The calibration process uses the linear regression factor as a multiplier for the net peak area as reported by Bruker's *Artax* software for the spectra exported from *S1PXRF* (Table 2). This calibration was derived from flat metal samples and would not therefore be expected to be valid for analysis of an irregular surface of weathering products on ceramics. The numerical values obtained are purely indicative and not quantitative.

The analysis was conducted in March 2018 and was commissioned by Jon Hoyle of Gloucestershire County Council.

Results

General description of the assemblage

The assemblage investigated here comprises a collection of fragments of technical ceramics from context (119) (Table 1) and a piece of fired clay from context (312).

The analysed material from context (119) comprised 15 pieces out of a total of 24 fragments of technical ceramic in a fine, mostly pale grey, micaceous fabric. The fabric was similar in all classes of material. The 15 pieces comprised seven sherds of cupel, two sherds that were probably from cupels, two sherds from either cupel or crucible, one crucible lid fragment and three fragments probably from moulds.

The sherds interpreted as deriving from large cupels form the focus of the analytical work and include several examples (119-1, 119-2, 119-3, 119-4, 119-7 and possibly 119-9). Typically, cupels were employed to dissolve small quantities of alloy in molten lead under an oxidising blast. The base metals dissolve in the lead and become captured by the reaction of the litharge (lead oxide) with the ceramic substrate. The silver in the alloy remained unreacted, forming a 'button' of metal in the centre of the cupel. The reaction between the litharge and ceramic typically produced a brown glaze.

The present material does not exhibit such a glaze, instead showing a granular greenish dross both on the surface of the cupel. Where the cupel surface was not covered in the dross, there was commonly a thin cream-coloured film over the ceramic surface. There were two occurrences in which the dross was observed to contain small prills of bright metal, probably silver.

In three examples, the cupel had been relined (in one case at least twice), with a thin (1.5 to 2 mm) layer of silty clay spread over the pre-existing dross remnants.

These cupels belong to a class of vessels which were commonly known as 'heating trays', but more usually now as cupels. Roman examples commonly lack the development of a deep lead glaze, as commonly seen on early medieval examples, and lack the reactive lining employed on medieval and later cupels. None-the-less, their use was the same as for the more developed types of cupel. The form best evidenced in the Kyrleside assemblage is (Figure 1a) a vessel with an internal depth of 20-30mm and a diameter of approximately 100mm, with thick, steeply splayed walls. Thy are hand-made, and rather irregular in shape (precluding more precise reconstruction of their dimensions). They are a very common form and may be compared for instance, at least in general form, with relatively local examples from Caerleon (Zienkiewicz 1993, Figure 46).

A thin dark film was observed on one thinner sherd of either cupel or crucible. One small sherd (119-13) showed a vitrified and slightly crazed or fissured surface, suggestive of being from a crucible.

One large piece (119-5) is interpreted as part of an unusual asymmetric crucible lid (Figure 1b). It bears a central knob, or handle, through which passes a small perforation. Perforated crucible lids have been identified in crucibles interpreted as being from brass-making, although lids may occur in crucibles with other uses. This piece lacks the outer clay or lute coating that commonly seals the lids of such crucibles and it may not have been used.

Just three examples of possible mould fragments were analysed. One was a typical small fragment with oxidised outer surface, one a tiny example of a possible sprue-cup and one a reduced fired clay fragment with the partial impression of three lobes, possibly suggestive of the head of the bow of a brooch and wings to cover the spring, but poor preservation precludes certain identification.

Details of the archaeometallurgical residues

The raw net peak area data is presented in Table 2 and an approximate indication of the relative concentration of the major metals in Table 3. The analyses made on areas of dross show extremely variable relative proportions of copper, zinc, lead, tin and silver. One analysis (119c-i) showed lead with low levels of silver. High levels of tin were demonstrated by four of the nine dross analyses and all showed moderate levels of copper and zinc. Silver was present

(where detectable) in low proportions, but highest where lead was the dominant metal (analyses 119-4, 119-8).

Analyses of examples of the thin cream-coloured film present away from the areas of dross (119c-g, 119c-h) show high proportions of zinc (probably largely present within the body of the ceramic; Kearns *et al*. 2010), together with lead and tin, typically indicative of the more oxidised part of the mixed assemblage.

Fragments of external surfaces show only slightly elevated levels of zinc and lead.

Analyses of the crucible lid (119l-j, 119l-k) showed only a very slight apparent relative enrichment in lead, but not of zinc. The lid appears very fresh, and since such lids were typically luted on to the body of the crucible, it is possible that this example was unused.

The possible mould fragments (119m-l, 119m-m, 119c-y) showed little conclusive evidence for metal contamination, except for the possible brooch mould fragment, which showed elevated levels of zinc (119c-u).

The analyses of the fired clay from context (312) showed no evidence for enrichment of metals.

Interpretation

Despite not being classic, glassy, cupel residues, the dross present on the inner surface of the cupels shows variation from dominantly lead oxides (with some silver) through to compositions of approximately equal proportions of copper and tin, with lesser amounts of zinc, mixed with some lead. This apparent end-member of the analyses does not represent a likely 'real' copper alloy composition (for the copper content is too low), nor does it appear to be the base metal component of debased silver coinage (which is typically a copper-silver alloy, low in both tin and zinc). This composition would appear to have been highly modified as a result of the oxidation process, coupled with a degree of alteration.

The metal being processed in the cupels appears, at least in bulk, to have been a copper alloy, rich in both tin and zinc. Because the material would have been mixed with lead in the cupellation process it is not possible to determine if the initial copper alloys were also lead-bearing. The evidence would be entirely compatible with the precursor metal being gunmetal or leaded gunmetal.

If the nature of the precursor metal is not certain, the pattern of lead distribution appears more certainly to confirm the cupels as having been used for desilvering. The desilvering is likely to have been part of a recycling process. The unusual precursor composition might have been due to the recycling of mixed scrap from the workshop. The only evidence for the objects being cast at the site producing this waste is the tentative evidence for moulds for brooches.

The nearby site at the Water Treatment Works, Dymock (Catchpole 2007), provided much more comprehensive evidence for an operation involving the production of copper alloy brooches with a white metal, probably silver, coating (Dungworth 2007). The residues from Kyrleside are very likely to represent residues from a similar activity. The cupels examined for this report might have been employed to extract silver from recycled materials brought in for the purpose, or perhaps to recycle waste materials generated within the operation.

References

CATCHPOLE, T. 2007, Excavations at the Sewage Treatment Works, Dymock 1995*, Transactions of the Bristol and Gloucestershire Archaeological Society*, **125**, 137-219.

DUNGWORTH, D. 2007. Slags and Moulds. *In*: Catchpole, T. 2007, Excavations at the Sewage Treatment Works, Dymock 1995, *Transactions of the Bristol and Gloucestershire Archaeological Society*, **125**, 183-186.

KEARNS, T. MARTINON-TORRES, M. & REHREN, T. 2010. Metal to mould: alloy identification in experimental casting moulds using XRF. *Historical Metallurgy*, **44**, 48-58.

NICHOLAS, M & MANTI, P. 2014. Testing the applicability of hand held portable XRF to the characterisation of archaeological copper alloys. *In* J. Bridgland (ed) *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014. Paris*: International Council of Museums.

YOUNG, T.P. & KEARNS, T. 2010. Evaluation of metallurgical residues from Kyrleside, Dymock, Gloucestershire (32523 & 33787). *GeoArch Report 2010/1*9.

ZIENKIEWICZ, J.D. 1993. Excavations in the *Scamnum Tribunorum* at Caerleon: the Legionary Museum site 1983-5, *Britannia*, **24**, 27-140.

Figure Captions

Figure 1: idealised reconstructed forms of (a) a thick walled cupel, and (b) the crucible lid (119-15).

Figure 2: images of the analysed sherds to assist in their identification for drawing.

Table 1: summary catalogue of technical ceramics from context (119)

#	notes
	Thick-walled cupels
119-1	sherd 60x45mm in plan, with flat interior c30mm diameter; side preserved to 15mm height above interior base on one side extending 18mm outside flat area; base >14mm thick, but external surface not seen; shows evidence for one and probably two relinings, each coated by thin dross layer, to local total thickness of contents of 5mm; wall 13mm thick at 10mm below rim
119-2	fabric, shows external smooth micaceous surface, below which maximum of 12mm slightly oxidised, up to 10mm grey reduced cermaic and up to 5mm contents resting on inner surface; contents apparently single dross layer; 38mm of external height and 20mm internal height preserved; base not seen; vessel probably >90mm diameter
119-3	vessel probably c100mm diameter; shows c1.5mm thick internal buff relining, over layer of green metal droplets; external face slightly angular 10mm below rim; 24mm of internal height seen; wall 16mm thick at 10mm below rim.
119-7	rim 13mm thick 10mm below top, up to 7mm dross with at least one relining event; dross and vitrification extends to top of rim
119-9	slightly more angular rim than typical; 12mm thick 10mm below rim, dross mostly high on rim, locally extending over top
119-10	thick walled cupel, 12mm at 10mm below rim, clean of dross but discoloured; 18mm internal height preserved
119-13	abraded thick cupel sherd with dark residue on internal surface
119-15	sherd from close to rim of thick-walled cupel; patchy pale and dark residues on internal surface
119-16	large sherd of thick walled, splayed cupel, no visible residues, possibly unused, 28mm height preserved, base missing; estimated diameter 100-120mm
119-17	sherd of thick walled cupel, internal surface spalled away external present to rim.
119-18	part of external face of thick-walled cupel, spalled from inner parts
119-22	probable spall from external surface of cupel
119-23, 24	two fired clay fragments, probably debris from a cupel
	Thin-walled cupels and crucibles
119-4	thin walled (6mm at 10mm below rim), very irregular; vessel 60mm in diameter approximately; inner surface vitrified and vesicular.
119-5	probably asymmetric crucible lid; knob 18mm diameter, with 3mm diameter slightly oblique perforation; probably covered vessel 40mm x 55mm; knob 8mm from one end; 26mm tall; same grey micaceous fabric as cupels, not obviously used
119-8	steep walled crucible/cupel; 8mm thick 10mm below rim; dark interior residue with white metal droplet embedded in cermaic above limit of slag
119-12	thin sheet of slightly vitrified clay with a mildly fissured surface, possibly a crucible fragment
119-19	deformed rim from splayed crucible or thin walled cupel; rim split and fissured; some brown external deposits/glaze, suggests this may be a crucible
119-20	tiny fragment with similar external brown colour to 119-19
119-21	possible thin crucible sherd, but might be spall from exterior of cupel
	Moulds
119-6	a tiny mould fragment has an oxidised exterior; the internal surface shows a small part of the matrix suggestive of a cylindrical curved surface, 5mm radius, preserved for a length of 14mm.
119-11	small concavo-convex grey silty ceramic fragment, with trilobed internal impression suggestive of poorly preserved mould matrix. Trilobed form hints at brooch head, but not certain.
119-14	tiny fragment of cup-shaped cermaic, external oxidised, probably a tiny sprue cup from a mould

Table 2: net peak area as reported by Bruker's Artax software for the spectra exported from S1PXRF.

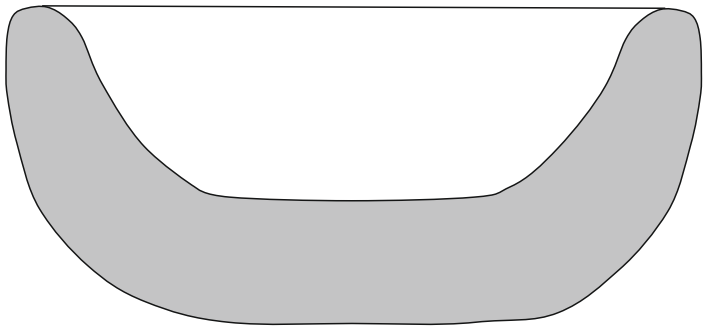
Element	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Rh	Rh	Ag	Ag	Sn	Sn	Sb	Sb	Pb	Pb
Line	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	L1	K12	L1	K12	L1	K12	L1	L1	M1
119c-a		73789	1105	145	441868	176879	1037	1343	5301	1899	9783	82			85864	295	394	834	163696	116
119c-b		177267	2230	509	219022	381402	1860	2257	9991	3137	18362	70	2289	534	306450	1086	404	1585	332210	489
119c-c		172113	1847	557	373025	695928	1232	1586	9608	2584	16604	59	2821	549	199179	1678	350	1478	334052	282
119c-d	5746	195593	2064	379	144123	577437	1467	2892	9232	3506	17536	35			233188	1553	623	1387	294364	282
119c-e		264924	2738	152	280751	348045	1993	3772	5688	7648	18936	84			89478	989	367	2304	144382	160
119c-f	2868	267071	2298	488	19301	121165	5344	8693	4431	31381	29873	84			2292	324	605	1268	12807	82
119c-g	1472	162410	1516	326	82549	584995	2358	3299	7534	11963	17432	141			87497	289	138	1067	139327	154
119c-h	1514	173099	1522	332	149606	1269273	2099	2524	7028	8224	19092	70			149306	564	121	1252	174752	200
119c-i	1337	121942	1153	183	37069	9039	4377	6204	15537	9558	18003	127	33913	590	11254	152	-36	1646	1147428	218
119m-l	2041	159144	1705	394	16972	8220	6534	7786	2868	22672	22535	33			1077	338	684	1095	8276	80
119m-m	2623	228093	2215	417	14553	10386	7009	8867	3395	26437	26945	88			1518	441	288	1075	10868	123
119c-n	1972	170683	1936	487	468805	320653	2263	2963	14543	3183	19728	103			316302	928	505	2269	575344	445
119c-o	2205	224971	1749	333	219979	891003	2819	2278	4859	8112	17229	59			31337	284	318	1097	95028	157
119c-p	1952	337486	3661	236	95895	11022	5669	6817	15270	11139	20895	103	83361	657	13001	124	14	2554	837584	170
119c-q	1850	120171	1212	343	679631	707527	1873	2371	7539	4883	15120	58	4037	643	103618	606	677	1567	212856	223
119c-r	2583	207021	1649	458	140998	1396002	2406	3277	3926	10416	18340	134			11758	449	558	1551	63978	122
119c-s	2301	158999	1425	456	130822	1734894	3636	3455	2794	13302	19331	104			7285	383	433	2354	25266	123
119c-t	2443	161566	1320	198	55205	1989039	1983	2471	3020	9525	17000	133			3028	210	272	1709	28905	165
119c-u	2963	178562	1610	361	11697	424146	4294	4337	2672	18721	20306	46			2666	287	226	1001	9134	96
119c-v	2315	193002	1667	352	76520	1906185	2047	3062	3503	10347	18097	139			12068	330	456	1608	41589	134
119c-w	2377	188343	1767	399	52682	1601978	2645	3413	3638	12329	18493	109			10274	217	75	1567	41422	118
119c-x	3187	212581	1929	480	7195	184238	5688	6623	3307	27346	24486	27			1396	317	261	1063	5666	129
119c-y	2789	202556	2121	380	14197	83030	6332	8228	3393	22824	24210	87			1078	358	180	1002	8661	42
119c-z	2190	188768	1674	235	31334	139306	6455	3886	2977	17776	17775	36			887	335	301	950	14916	148
312a	6558	333772	2820	175	1478	2174	5953	11546	3277	17829	23335	52			1064	420	435	1577	2248	14
312b	5718	339838	2901	245	1608	2337	6595	13315	4094	19662	25897	13			1568	475	490	1688	2500	46

Table 3: list of analysed material, with qualitative analyses (indicative only) of significant elements in wt%.

piece	notes	analysis	Fe	Cu	Zn	Sn	Pb	Ag
	dross							
119-1	large cupel fragment; Cu-alloy dross	119c-a	1.3	7.8	2.2	5.9	7.0	
119-1	dark dross in centre of bowl	119c-b	3.1	3.9	4.7	21.2	14.1	0.1
119-1	dross on edge of central area	119c-c	3.1	6.6	8.6	13.8	14.2	0.1
119-2	dross just below rim	119c-d	3.5	2.5	7.1	16.1	12.5	
119-2	dross on lowest part of side	119c-e	4.7	4.9	4.3	6.2	6.1	
119-4	dross on small sherd	119c-i	2.2	0.7	0.1	0.8	48.8	1.4
119-7	surface of thick dross on stout rim	119c-n	3.0	8.2	3.9	21.9	24.5	
119-7	cross section of thick dross	119c-o	4.0	3.9	11.0	2.2	4.0	
119-9	dross blebs attached to inner face of rim sherd	119c-q	2.1	12.0	8.7	7.2	9.0	0.2
	thin dark residue							
119-8	dark residue on small sherd of thin cupel/crucible	119c-p	6.0	1.7	0.1	0.9	35.6	3.3
	clean or cream residue							
119-3	cream inner surface - upper part of face	119c-g	2.9	1.5	7.2	6.0	5.9	
119-3	cream inner surface - lower part of face	119c-h	3.1	2.6	15.6	10.3	7.4	
119-9	inner surface between blebs	119c-r	3.7	2.5	17.2	0.8	2.7	
119-10	inner surface of clean cupel rim side at rim	119c-s	2.8	2.3	21.4	0.5	1.1	
119-10	inner surface of clean cupel, towards lower wall	119c-t	2.9	1.0	24.5	0.2	1.2	
119-12	cream and dark film on small cupel sherd	119c-v	3.4	1.3	23.5	0.8	1.8	
119-12	cream and dark film on small cupel sherd	119c-w	3.3	0.9	19.7	0.7	1.8	
119-15	small cupel sherd, planar, traces of dark residue	119c-z	3.3	0.6	1.7	0.1	0.6	
	external and lid							
119-2	external surface	119c-f	4.7	0.3	1.5	0.2	0.5	
119-5	lid rim surface	119l-j	4.3	0.1	0.1	0.1	0.5	
119-5	lid around perforation	119l-k	3.3	0.1	0.1	0.1	1.1	
119-13	tiny sherd with fragmented inner face	119c-x	3.8	0.1	2.3	0.1	0.2	
	moulds?							
119-6	tiny mould fragment internal	119m-l	2.8	0.3	0.1	0.1	0.4	
119-6	tiny mould fragment external	119m-m	4.0	0.3	0.1	0.1	0.5	
119-11	inner face, corrugated surface, possible mould, brooch head	119c-u	3.2	0.2	5.2	0.2	0.4	
119-14	inner face of tiny possible sprue cup	119c-y	3.6	0.2	1.0	0.1	0.4	
	amorphous clay							
312-1	dark surface of large fired clay lump	312a	5.9	0.0	0.0	0.1	0.1	
312-1	As 312a	312b	6.0	0.0	0.0	0.1	0.1	

Figure 1

a



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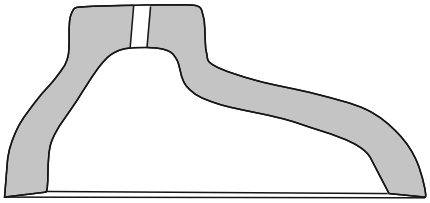
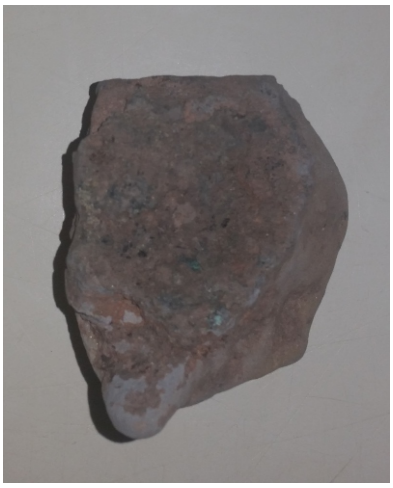


Figure 2

119-1



119-2

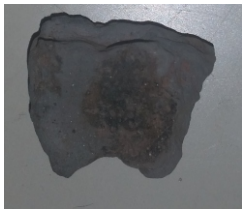
119-3

119-4

119-5

119-6

119-7



119-8

119-9

119-10

119-11

119-12

119-13

119-14

119-15

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