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Archaeometallurgical residues from St Patrick's Chapel, Whitesands Bay, Pembrokeshire

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Abstract

Semi-quantitative elemental analyses were made by handheld portable-XRF (pXRF) on a selection of probable archaeometallurgical residues recovered during excavations at St Patrick's Chapel, Whitesands Bay, Pembrokeshire. The material included one fragment of slag, two small corroded blebs of metal, three sherds of crucible, four assorted non-metallurgical materials and twenty-one fragments of cermaic mould.

The metallurgical assemblage was compatible with having been generated during a short episode of casting copper alloy (probably a very lightly leaded bronze) to produce small artefacts in two-piece moulds. The materials are probably of early medieval age.

Although very variable in composition, the residues were all compatible with generation from broadly the same alloy composition. Most of the mould fragments showed evidence for enrichment in copper, tin, lead and zinc. Lead, copper and tin were typically concentrated in the inner parts of the mould close to the matrix, whereas zinc had permeated through the mould as vapour and was preferentially enriched towards the outside of the cermaic. Modelling of the metal composition tentatively suggests a tin bronze, with less than 1% of zinc and a few percent of lead. Such a metal would be classifiable as a bronze, or a leaded bronze, depending on the scheme used.

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Methods

The material described here derives from excavations at St Patrick's Chapel, Whitesands Bay, St Davids, Pemborkeshire, by Dyfed Archaeology.

This report details analytical investigations undertaken with a handheld portable X-Ray Fluorescence instrument; morphological and typological reporting on these residues is to be undertaken by Dr Mark Redknap, National Museum Wales. 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 from two highly corroded metal blebs 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. This calibration would not be expected to be fully valid for analysis of an irregular surface of weathering products, rather than smooth metal, hence it is not a fully quantitative approach. The calibration process uses the linear regression factor as a multiplier for the net peak area as report by Bruker's *Artax* software for the spectra exported from *S1PXRF* (Table 1).

Results

Description of the residues

The assemblage comprises a large collection of highly fragmented cermaic moulds, together with a small number of crucible sherds corroded blebs of metal and fragments of slag. A selection of materials was subjected to analysis by pXRF. Full description of the ceramic materials will be the subject of a separate report to be provided by Dr M. Redknap; accordingly, only a summary note on the residues is included here.

Slag: a single fragment of slag was analysed (context (129), find #439). The slag was glassy, dominantly greenish, but with some reddish areas, with indications of flow down a steep surface. The rear of the slag piece was sandy, possibly indicative of the nature of the hearth wall.

Metallic blebs: context (129) also yielded (as find #435), two small highly corroded blebs of metal. The blebs were bright green in colour with coarse crystals of secondary copper minerals protruding from their surface.

Crucibles: three sherds of crucibles were analysed, two from find #436, one from find #421, all from context (129). The fragments were from medium-sized triangular crucibles. The outer surfaces were coated in a thick glaze, locally with of a transparent green, but more generally of an opaque strong red. The inner surfaces were matt and dark grey. The fabric was fine-grained.

Moulds: the mould fragments were mostly fine grained and showed a variety of patterns of oxidation. Wherever identifiable, they are all fragments of piece moulds (bivalved moulds created around a former, which is removed and the inlet gate sculpted), rather than being investment moulds (from the lost-wax process).

The most common form was strongly reduced, with just a very thin (1mm or less) oxidised-fired (buff/orange) external zone. Other materials showed more oxidation, with a significant number showing dark grey oxidised fabrics throughout. Some of the pieces were identified as large (c. 20mm diameter) location bosses (keys), together with a few examples showing the corresponding recess from the opposite valve. All of these key fragments were entirely oxidised. Only a very few fragments showed evidence for the original matrix. A very few fragments showed visible carbonaceous or altered metallic residues adhering to the face of the mould. The moulds were characterised by mostly being very thin (typically less than 12mm).

Analysis of the residues

The net peak areas for selected peaks are presented in Table 1. Figure 1 illustrates the variation in the net peak areas of the principal components of the alloys being cast: copper, lead, tin and zinc.

Some non-metallurgical materials were analysed in order to determine the background levels of the various metals within objects from same contexts. These included a bone fragment (context (165), find #468), a mollusc shell, probably a winkle (context (160), find #471), and a piece of iron-rich siltstone (context (160), find #471). In addition, a small fragment of tempered fired clay (oxidised fired, with both coarse quartz and hair temper) that may also possibly be non-metallurgical, was also analysed (context (165), find #468). These all proved to have low levels of copper, zinc, tin and lead.

Some indication of the original metal composition is provided by the analyses of the slag, crucibles and most particularly the corroded metal blebs. Of these,

only the corroded blebs might be able to provide an analysis that approximates to that of the original metal. Because of the irregular nature of these corroded blebs, and their weathered state, only a very approximate analysis can be obtained by pXRF. Furthermore, the calibration applied to the analysis here is only capable of a crude approximation to the actual composition, because it is derived from work on large polished planar metal surfaces. In addition to the poor quality of the analysis, there is uncertainty as to whether there has been any change to the elemental composition of the spill during weathering (by preferential leaching, for instance). The composition of corroded casting spills is also unlikely to be completely representative of the original bulk metal being cast. Thus, at several levels, the analysis presented here is likely to be poor approximation to the original metal composition. Nonetheless, Table 2 presents some modelling of the composition of the blebs.

The corroded nature of the blebs is reflected in their low total of metals in the raw calibrated data. Normalising the metal data to 100% shows a large difference between the two blebs, but comparison of the data excluding copper (right hand columns of Table 2) reveal the variation to be different contents of copper, with the other elements (zinc, tin and lead) in a similar ratio to each other in the two blebs.

Classifying the metal on the basis of such low-quality analyses is fraught, but the general impression is that zinc is low (probably around 1% or less), tin is high (eight to nine times the concentration of zinc; perhaps in the range indicated by the estimates of 4 and 10%), and that lead is moderately high (four to five times the concentration of zinc; perhaps in the range indicated by the estimates of 2 and 6%). The metal may probably therefore be classifiable as a bronze, although the term 'leaded bronze', usually employed for bronzes of greater than 8% lead (Bayley & Butcher 2004, 14), but sometimes for bronzes with as little as 1% lead (Pollard *et al* 2015, 700), might be applicable. If the zinc were to have been as high as 1%, then the material could be considered as close to a composition transitional between a bronze and a gunmetal.

Alloys of this quaternary composition are usually considered as indicators of recycling. The low zinc content is typical of metal in circulation in the early medieval period (post-'early Saxon'; Blades 1995), in which the higher zinc metals of earlier periods have become diluted and have undergone zinc loss during recycling. The work of Blades (1995) demonstrates, however, how a wide range of alloy compositions can be found in all periods.

The pattern of metal distribution within the twenty-one examples analysed of the material identified as mould fragments, proved to be distinct, and confirmed the debris as moulds. Both copper and lead show preferential concentration on the face of the fragments identified as the inner (matrix) face (typically reduced-fired). Copper is probably a simple contaminant in these materials (and occurs at much lower concentrations than in the slags, crucible and metallic blebs), but lead typically shows a strong reaction with silicate materials. The lead peaks in the pXRF spectra of the inner faces of the moulds were commonly larger than those of the crucibles, slags and even the metallic blebs. Zinc, in contrast, is typically transferred from the hot metal in the vapour phase (Kearns *et al.* 2010), and this shows greatest enrichment in the outer parts of the moulds.

Discussion

The composition of the original metal cannot be determined with any certainty, but was probably a bronze, bearing some zinc and lead and therefore close to being a gunmetal. Such a metal would be considered a typical general-purpose material for small castings.

None of the ceramics in the assemblage gave any evidence for being involved in the handling of precious metals, and the assemblage is unusual in containing no residues from ferrous metalworking.

The technologically restricted range of the assemblage is paralleled by its stratigraphic restriction. This is very likely to suggest that the metalworking debris is the product of a single short period of activity, rather than a more typical long-lived craft.

The form of the crucibles, the mould technology and the metal composition are all compatible with an early medieval age.

Further work

It is possible that further revisiting of the analytical data to provide information on individual moulds, when a degree of reconstruction has been attempted, may be useful.

References

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Figure Captions

Figure 1: binary plots of the net peak area for zinc (upper), lead (middle) and tin (lower), plotted against copper for pXRF analyses. Symbols indicate the various residue types.

Table 1: net peak area for selected peaks, as calculated by Artax.

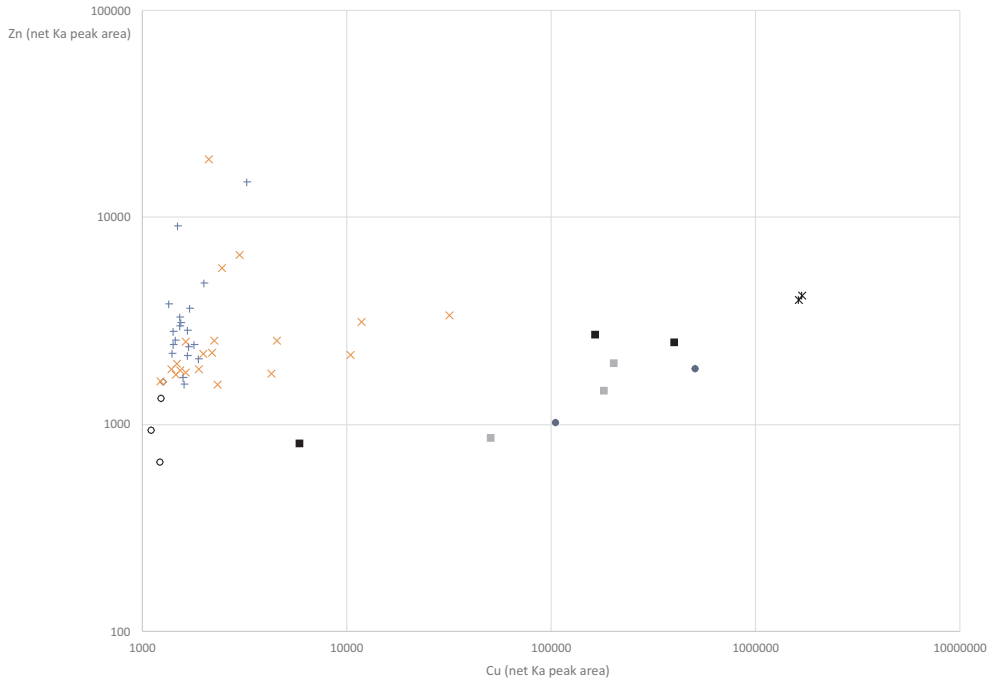
sample	context	piece	Element	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Rh	Sn	Pb
			Line	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	L1
			Energy/keV	3.692	4.512	5.9	6.405	6.931	7.48	8.046	8.637	13.396	14.165	14.958	15.775	20.216	25.271	10.551
421	129	1	crucible #1	18663	3197	8405	233125	1487	21	182104	1452	3134	23021	2742	17231	29200	5578	1092
421	129	1	crucible #2	23045	2410	14976	161127	939	57	203211	1982	2485	27054	2492	15236	25565	11698	983
421	129	1	crucible #3	6292	815	2972	62065	816	238	403256	2482	1344	3032	950	8463	15392	21064	1406
434	129	1 (left)	ceramic 1 buff #1	13151	2771	3197	173746	877	69	1523	2994	4478	6234	3095	19076	27046	836	899
434	129	1 (left)	ceramic 1 grey fracture #1	4435	1921	3044	121107	659	68	1279	1848	2934	4151	2577	14858	22940	1509	2912
434	129	2	ceramic 2 grey matrix #1	3723	2731	1963	129447	1036	90	1476	1986	3714	24995	2861	19384	28244	1596	3929
434	129	3	ceramic 3 darkest grey side matrix #1	5223	2425	3677	150569	994	1	1532	1829	3525	4709	2843	18724	26794	1022	959
434	129	3	ceramic 3 pale grey side #1	4011	2657	2899	166138	1218	40	1525	3321	3625	6014	3155	19144	26248	1354	953
434	129	4	ceramic 4 darker grey side convex #1	11328	4370	6594	253688	2046	334	1629	2514	7789	23393	2822	23512	26664	1390	1667
434	129	4	ceramic 4 paler flat side #1	5472	4649	5545	260382	1737	326	1421	2429	7317	17460	2702	22541	25253	1211	1360
434	129	5	ceramic 5 darker convex side #1	4462	3046	4142	201126	1237	91	1545	3123	4435	4480	3114	20009	29060	1121	1093
434	129	5	ceramic 5 paler convex side #1	2750	2497	3513	155519	1229	80	1212	1635	3874	4681	2840	19478	25929	1282	821
434	129	6	ceramic 6 broken oxidised outer face #1	12230	2882	3707	181464	957	95	1399	2215	4223	5018	3422	23453	27832	1348	1099
434	129	6	ceramic 6 darker planar side poss matrix #1	4424	2441	2679	148332	974	77	1454	1759	3441	4998	2614	17504	24628	888	2080
434	129	7	ceramic 7 buff #1	3854	2686	3118	175321	1105	122	1349	3834	4120	5537	2913	18665	25842	1676	772
434	129	7	ceramic 7 orange #1	3868	3011	3006	172203	932	14	1627	1791	5342	5849	2974	21673	28786	1215	838
434	129	8	ceramic 8 orange boss to front #1	4998	3074	4111	192756	1522	63	1888	1865	4305	5357	3276	19666	29832	1644	2925
434	129	8	ceramic 8 orange broken rear #1	3015	2694	2719	184706	1177	115	1584	1693	4485	5517	2887	20041	27214	1463	1217
434	129	9	ceramic 9 orange boss hole to front #1	3395	2881	2840	180919	953	56	1371	1852	4298	5470	2910	18983	28210	990	620
434	129	9	ceramic 9 orange planar rear #1	2816	2775	3196	184808	1021	80	1482	9156	4778	5494	3588	19639	27803	1522	788
434	129	10	ceramic 10 buff darkened possible matrix #1	7385	2267	2899	162872	1180	91	10351	2180	4206	4037	2706	18048	26689	2543	4060
434	129	10	ceramic 10 buff planar but rough rear #1	6610	3070	2905	175948	1224	126	1422	2824	4409	4698	2813	21564	26350	1435	780
434	129	11	ceramic 11 inner smooth grey	4297	2724	3089	231392	1456	117	11683	3133	3793	4197	3231	19263	25597	3670	7712
434	129	11	ceramic 11 outer rough thin orange	10806	2550	3059	191448	1199	50	1668	2150	5731	6676	2730	20169	26953	1411	536
435	129	1	bleb #1	3532	441	566	26591	529	527	1679930	4204	338	1429	340	581	8000	19234	766
435	129	2	bleb #2	2047	264	286	11264	408	1191	1618387	4020	341	748	222	263	6708	27025	1810
436	129	1	inner lip crucible #1	6670	1093	3285	80193	551	80	163462	2729	1392	5096	1219	7446	11111	14250	1092
436	129	1	red glaze mid body crucible #1	21550	1717	14698	157341	947	68	50888	860	3203	39625	2186	14593	26842	1605	332
436	129	2	inner small fragment crucible #1	2987	1343	2106	100802	668	97	5853	808	3056	2613	1808	11905	19167	1713	816
439	129	1	slag exterior vitrified surface #1	6831	1431	9835	59900	510	39	104705	1028	3345	21909	1288	13205	16265	10897	941
439	129	2	slag sandy rear surface #1	10945	1482	2972	71153	840	593	509549	1868	1794	13922	440	3457	19154	52041	2762
437	131	1	ceramic 1 dark face #1	3654	5405	5426	261647	1712	337	2238	2545	8229	22052	2877	24542	26343	1169	1677
437	131	1	ceramic 1 orange face #1	6416	5010	5591	296425	2231	454	1665	2848	8146	18975	3110	26370	26632	1868	1193
437	131	2	ceramic 2 dark face with boss hole #1	4133	5892	8271	284271	1801	374	1963	2216	8344	18189	2940	25209	27415	1234	1525

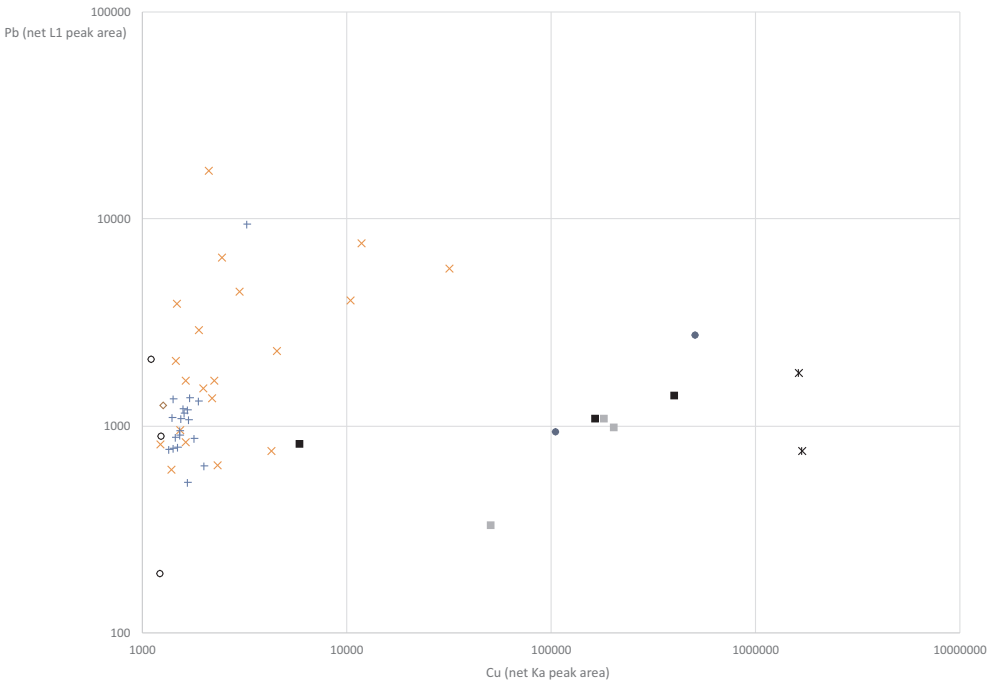
sample	context	piece	Element	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Rh	Sn	Pb
			Line	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	L1
			Energy/keV	3.692	4.512	5.9	6.405	6.931	7.48	8.046	8.637	13.396	14.165	14.958	15.775	20.216	25.271	10.551
437	131	2	ceramic 2 orange outer face fracture #1	32377	2970	6512	187778	1396	262	1595	1562	7023	17344	2347	20021	21331	754	1149
437	131	3	ceramic 3 inner	5755	5412	5074	272547	1660	366	2438	5697	7861	23255	3131	22512	25708	1354	6577
437	131	3	ceramic 3 outer	3381	4898	5289	289178	1800	340	1674	2378	8138	18556	2967	24337	25459	1202	1079
470	139	1	ceramic inner face	4448	4868	5193	284254	2022	329	2193	2241	7358	20847	2699	24008	25966	1231	1367
470	139	1	ceramic outer face	3201	4699	5089	255371	1647	297	1796	2427	7430	15788	2434	23135	24659	1354	876
455	154	1	ceramic 1 pale buff rear #1	2550	2530	2182	172303	1115	110	1456	2558	3916	3665	2928	17892	26897	889	884
455	154	1	ceramic 1 pale buff with green adhesion	3791	2586	2661	183663	1175	117	31825	3387	3530	4152	2781	16885	26103	2430	5833
472	156	1	ceramic 1 buff #1	2231	2493	2123	166147	1212	71	2325	1570	4070	4203	2426	16629	23863	928	649
472	156	1	ceramic 1 orange #1	3503	2669	3215	198038	1342	84	2001	4838	4826	4659	3276	22949	27302	1080	643
472	156	2	ceramic 2 pale buff tiny #1	6601	2794	3159	191666	1391	111	1884	2090	4441	9015	3124	20924	29659	1388	1319
472	156	2	ceramic 2 pale buff tiny #2	7079	2570	3338	165622	735	73	4240	1768	3657	6825	2328	17010	24565	1677	761
471	160	1	possible shell outer #1	199354	618	2986	43515	209	71	1217	660	238	85262	217	1702	27271	1228	193
471	160	2	red siltstone piece	8075	1710	97235	1216914	7642	282	1102	943	592	11717	1845	2015	21041	632	2098
468	165	5	bone	95625	711	23988	14030	-1	109	1226	1342	571	29534	165	1500	22242	547	896
468	165	4	tempered oxidised clay broken face #1	2929	2824	2034	183220	1062	48	1264	1601	4345	7410	2300	17959	25679	891	1265
468	165	3	small sherd grey side #1	8412	3879	4250	244072	1730	215	2105	19254	4841	14202	2413	16623	21766	1803	17243
468	165	3	large sherd orange side #1	5407	5171	6982	296328	2311	410	1710	3627	6899	13611	2562	23491	26987	1565	1369
468	165	2	thick sherd flat side #2	6981	5212	5955	278514	2090	268	3247	14949	5745	14907	2790	21078	24721	1484	9520
468	165	2	large sherd grey side #1	8129	5090	6904	282245	1805	342	2981	6677	6124	16443	2859	22512	27086	1514	4486
468	165	1	thick sherd broken edge #4	2395	2335	1638	146109	1014	115	2286	1280	3045	3156	2177	16661	23401	1384	856
468	165	1	thick sherd broken edge #3	26856	1960	8790	97961	506	104	4527	2567	3549	20868	1536	9724	27517	1972	2313
468	165	1	thick sherd broken edge #2	2111	2727	1753	177508	1047	126	2341	1564	3528	3612	2854	18277	25466	1368	994

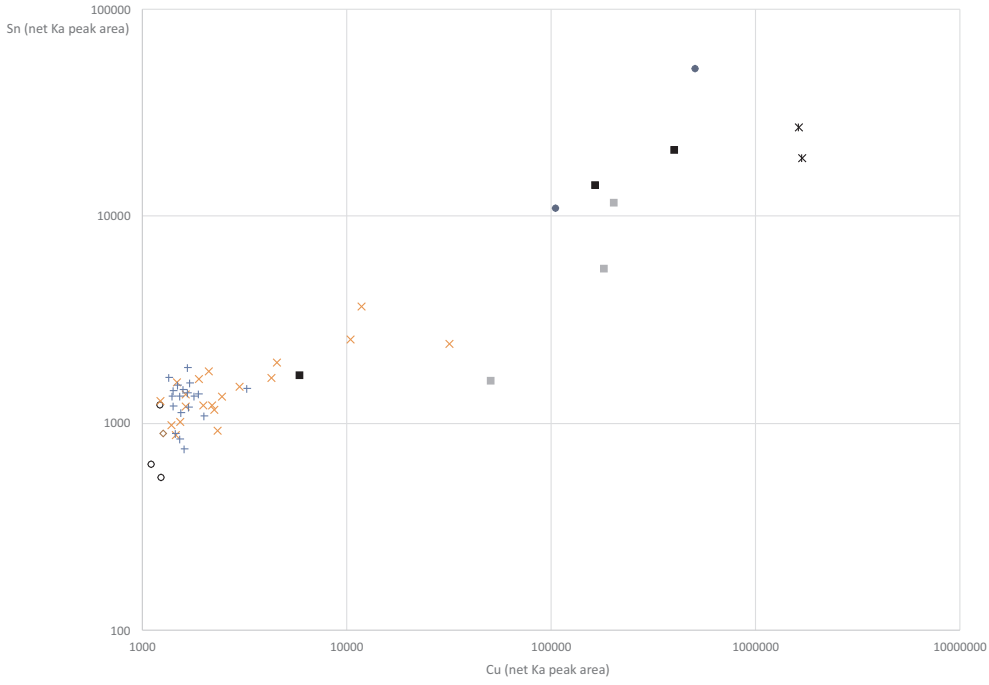
Table 2: semi-quantitative calibration of pXRF analyses of two corroded metal blebs from context (129) find #435.

Element	**Line**	**Net Area**		**Factor**	**Raw wt%**		**Wt% norm to 100%**		**non-Cu**	
		Bleb 1	Bleb 2		Bleb 1	Bleb 2	Bleb 1	Bleb 2	Bleb 1	Bleb 2
Ca	K12	3532	2047							
Ti	K12	441	264							
Mn	K12	566	286							
Fe	K12	26591	11264	0.00001773	0.5	0.2				
Ni	K12	527	1191	0.00001789	0.0	0.0				
Cu	K12	1679930	1618387	0.00001759	29.5	28.5	93.2	82.0		
Zn	K12	4204	4020	0.00001231	0.1	0.0	0.5	1.2	7%	7%
Sr	K12	1429	748							
Zr	K12	581	263							
Rh	K12	8000	6708							
Sn	K12	19234	27025	0.00006914	1.3	1.9	4.2	10.2	63%	57%
Pb	L1	766	1810	0.00004250	0.0	0.1	2.0	6.4	30%	36%

Figure 1







- non-metallurgical
- tempered clay
- slag
- blebs
- crucible internal
- crucible external
- mould internal
- mould external

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