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Archaeometallurgical residues from Topsham, Devon

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Abstract

Excavation of pit [1427] discovered a network of sub-vertical veins of weathered lead penetrating into the natural deposits below the pit cut. The most likely interpretation of these veins is that molten lead penetrated down desiccation cracks produced by heating in the overlying pit. The extent of the vein network across the whole of the cut of the 0.5m diameter pit would be extremely unlikely to have been generated by simple casting spills; rather the area of pit must have been substantially covered by molten lead.

Five potential interpretations are discussed:
- primary lead smelting,
- the casting of a large circular ingot,
- the purification of molten lead through formation of a dross under oxidising conditions,
- use of the pit as a cupellation hearth (in which case the large size of the pit would suggest bulk desilvering of fresh lead, rather than for recycling or assaying),
- the resmelting of litharge from cupellation.

In most of these cases, molten lead would have been in contact with the base of the hearth, whereas in cupellation the molten lead would have been oxidised with an air blast to litharge (lead oxide) which would then be absorbed by a lining rich in calcium (crushed shells, bone ash or plant ash for instance), leaving buttons of silver and a resmeltable cake of litharge. In either case the penetration of the lead into the subsoil would have been unintentional.

In an attempt to discriminate between these possibilities, bulk chemical analysis was undertaken on three samples: one from the top of a vein, immediately below the pit flor, one from the substrate immediately below the pit floor, and a third from the substrate some 60mm lower.

None of the three samples showed any evidence for strongly elevated contents of either calcium or phosphorus, as might be expected if they contained a significant quantity of lining of either bone ash or plant ash. The subsoil immediately below the floor of the pit is more aluminous than that deeper down, and shows just very slightly elevated contexts of iron, calcium, magnesium and potassium; it is likely that this reflects a more-clay-rich composition of this layer. The non-lead component of the lead vein is even more aluminous, with calcium and phosphorus very slightly elevated (in a proportion compatible with both bone ash and natural apatite), but to an oxide total of <4% of non-metal component. Potassium is depleted with respect to the subsoil.

The evidence suggests any bone- or wood-ash substrate cannot have been a major contributor to the materials. The non-metal content of the vein approximates to kaolinite rather than to any typical cupellation substrate. The nature of the process undertaken in pit [1427] therefore remains uncertain.

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Methods

Excavations in Topsham, Devon, by AC Archaeology (Site Code ACD 1360), revealed a Roman building, within the footprint of which was a shallow pit [1427], measuring c.0.5m diameter and 0.1m deep, with a charcoal-bearing fill. A sample of *Alnus*/*Corylus* charcoal has produced a 14C date of 135-345 cal.AD (SUERC-72546 (GU43786) for fill (1429).

The natural deposits below the base of the pit were cut by reticulate network of veins of lead and secondary lead minerals extending to depth of approximately 80mm below the pit floor.

Because of the unusual nature of the feature the entire excavated pit was subsequently block-lifted and stored. Following determination of an appropriate course of post-ex investigation, a section of the block was removed for analysis. Three samples were then removed from the block:
TOP1, a small piece of one of the veins, from close to the upper surface
TOP2, a piece of 'clay' from the upper surface of the piece, away from the veins,
TOP3, a sample of clay from the lower part of the samples, approximately 60mm below TOP2.

Bulk chemical analysis was undertaken using two techniques. The major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P) were determined by X-Ray Fluorescence using a fused bead on the Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) system in the Department of Geology, Leicester University (this also generated analyses for S, V, Cr, Sr, Zr, Ba, Ni, Cu, Zn, Pb and Hf).

Whole-specimen chemical analysis for thirty six minor and trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U) was undertaken using samples in solution on the ThermoScientific ICAP-Qc quadrupole ICP mass spectrometer (ICP-MS) in the Department of Geology, Leicester University (this also generates lower quality results for Fe, Mn, Ti, P that are used mainly for QA purposes). At the time of preparation of this report, the trace element data had not been returned by the laboratory, so the interpretation is based on the XRF data alone. An updated report will be provided once the additional data have become available.

The results of the chemical analyses are presented in Tables 1 and 2.

This project was commissioned by Alex Farnell, of AC Archaeology.

Results

Analyses are presented in Tables 1 and 2. Trace element data by ICP-MS are not yet available; an updated report will be provided as soon as they are.

Two analyses are presented for the high-lead sample TO1. The lead content was much higher than the calibration standards employed for the normal WROXI calibration programme. An alternative standard-less calibration is also presented, which provides a more accurate estimate of the lead. Other elements are believed to be best represented by the normal WROXI data.

Table 3 shows the major element analyses recalculated on a lead-free basis, enabling comparison with the estimated composition of the cupellation hearth linings as modelled by Dunster & Dungworth (2012, Table 5).

Girbal (2011) analysed and interpreted Roman and medieval litharge cakes using methodology developed by Martinón-Torres *et al.* (2009). They estimated the potential contribution from the bone-ash as the weight% P_2O_5 plus 1.2 times that percentage of CaO. Girbal (2011) modified that approach using a factor of 1.3 instead of 1.2 for empirical reasons. In this instance, the quantities involved are very small and a factor of either 1.2 or 1.3 effectively accounts for all the CaO, suggesting the carrier of both oxides is indeed an apatite, but reaching only approximately 3.4% apatite. Calculating the composition of a theoretical excipient (the non-ash component of the lining) gives a composition close to a mixture of iron oxide and kaolinite for the lead vein and decreasingly less aluminous compositions for the subsoil. Table 4 provides the chemical analyses modelled in this way.

Extrapolation from the very low level of contaminants in the lead vein is problematic and can only give a very crude model of what the material mixed with the lead may have been. It would appear, however, that the lead probably contained a component of kaolinitic composition, and that the top of the in-situ subsoil was richer in aluminous clay than a level 60mm below.

Interpretation

The development of the cracking/veining across the entire floor of the pit may suggest that the lead was introduced into the pit across its whole area. A simple casting spill into a hearth would be expected to be much more localised. Five potential alternative interpretations are possible:
- the collection of lead from a primary smelter,
- the secondary casting of a large circular ingot,
- the purification of molten lead through formation of a dross under oxidising conditions.
- the use of the pit as a cupellation hearth (in which case the large size of the pit would suggest bulk de-silvering of fresh lead, rather than for recycling or assaying),
- the resmelting of litharge from cupellation.

Primary lead smelting may employ a low-level pit to collect molten lead from an elevated hearth (Tylecote 1986, Figure 23). On a site with a moderate degree of truncation it is conceivable that the hearth might be entirely removed, leaving just the tapping pit. However, such an interpretation is unlikely for the present example, for the location is remote from sources of lead ore and no lead slag was recovered.

The casting of lead into a circular ingot might have been accomplished in a simple pit, perhaps with the use of a clay-rich lining. Tylecote (1986, 68) noted that the familiar primary trapezoidal Roman lead ingots were cast in clay moulds. Primary lead pigs (and also the pigs interpreted as having been desilvered) are elongate prisms, with a trapezoidal-cross section (Tylecote 1964; Todd 1996). Large circular lead ingots are not known – although it was the normal form for large ingots copper and tin ingots in the Roman period

(Fox 1996, Tylecote 1986). If the production of a circular ingot was the intention, then this is likely to have been for the purpose of recycling.

Purification of lead by drossing under an oxidising air blast has not been demonstrated for the Roman period, but is known from more modern settings (Percy 1870, 459). The most typical purpose for this process in recent times is the removal of antimony from raw lead. Antimony causes the lead to be hard and softening of the lead is desirable for many purposes. Analyses of British Roman lead ingots (Tylecote 1986, Table 38) show very low antimony contents, suggesting softening would not be required, even if the process were known.

If the present material is from cupellation, then the large size of the pit and the low copper content of the weathered metal suggest that it would have been from the processing of primary metal, rather than the recovery of silver from mixed alloys. Copper-bearing litharge cakes are relatively common on Roman sites and it is likely that recycling of non-ferrous alloys was commonplace. The previously-described modestly-sized litharge cakes from Exeter are likely to fall into this category (Bayley 1989a, 1989b).

Dunster & Dungworth (2012) indicated that only four sites have produced materials likely to be litharge cakes from the cupellation of freshly smelted lead: St Algar's Farm, Somerset (Dunster & Dungworth, 2012), Chew Valley, Somerset (Rahtz & Greenfield, 1977), Green Ore, Somerset (Ashworth & Palmer, 1957-58) and Pentreheyling, Shropshire (Bayley & Eckstein 1998). These localities are all close to locations of Roman lead-mining, but Topsham does not lie in such a location.

The secondary (recycling) litharge cakes analysed by Girbal (2011) show evidence for both bone ash- and plant ash-bearing linings. The analyses of primary litharge cakes of Roman age (Dunster & Dungworth 2012) are few in number, but do not indicate the use of bone ash – rather they indicate the use of clay and washed wood ash. If the present material is from cupellation, then a clay lining with a very low proportion of bone-ash may possibly be supported on the present evidence. The somewhat weak evidence for a former high-calcium content lining to the pit may reflect the genuine lack of such a lining – in which case it is possible that a different interpretation may need to be sought for the pit. The data show no conclusive evidence for the incorporation of pit lining into the floor of the pit or into the lead in the vein. The expectation would have been that any lining impregnated by litharge would have been completely removed after the processing of the lead, so no contamination of the underlying materials may simply mean that any lining was fully removed with the litharge cake (which would have been resmelted).

The resmelting of litharge from either primary or secondary cupellation processes might result in molten lead being collected in a pit below the hearth. The low levels of phosphate in the lead contained in the veins might be compatible with small particles of the bone ash in the litharge being carried with the molten lead produced by the smelting. There is no current archaeological evidence for the nature of either the materials associated with the process or the nature of the hearth/furnace within which it was conducted.

Discussion

The lack of materials associated with this hearth, except for the accidental leakage of lead into the cracked subsoil, provides significant barriers to its interpretation.

Although several potential originating processes have been identified, chemical analysis of the hearth floor and the lead veins has not provided an unambiguous solution.

Primary smelting is unlikely, particularly because of the location, as is oxidative drossing, but the resmelting of litharge and the remelting of recycled lead are both possible interpretations. These processes would not require a special lining to the pit. The cupellation of primary lead also remains a possibility, but would require all of the calcium-bearing hearth lining to have been removed with the litharge cake.

Further evidence for the nature of the lead working on the Topsham site might be forthcoming from careful consideration of any finds of lead metal from the excavation.

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Glossary

Cupellation
A process in which molten lead is oxidised, leaving any contained precious metals such as silver and gold, and metal. The oxidised lead (litharge) is typically drawn into an absorbent hearth lining, typically formed of calcium-bearing material, such as washed plant ashes, shells or bone ash. This lining can be removed (as a litharge cake) and resmelted to extract the lead. Litharge is strongly reactive with silicate materials to form a slag, so direct contact between such materials is avoided where the lead is to be recovered. The exception is when small-scale cupellation is undertaken for assaying purposes in a ceramic cupel – any contained silver is left as a metallic 'button' on the surface of the lead slag.

Cupellation may be undertaken to desilver primary lead, or as part of a process of separating the metals in mixed recycled scrap.

Desilvering
Lead minerals commonly contain silver, and are often associated with other silver-bearing minerals. Primary raw smelted lead may therefore contain significant quantities of silver. Various process for desilvering were employed in historical times, but in the Roman period desilvering would have been by cupellation.

Litharge
Another name for lead (II) oxide (PbO) and more generally for the product of oxidised lead, particularly that produced during cupellation.

Smelting
The processes of the primary production of a metal from its ore, by processes involving heating and chemical reaction.

Table 1: Bulk chemical analysis: major elements by XRF. < = below detection. All elements presented as wt% oxide.

	Calibration	Source notes	SiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Total
Top1	Normal WROXI	Top of crack fill	6.02	4.94	0.68	0.02	0.14	0.26	<0.016	0.22	0.06	0.20	14.74	125.63
Top1	Standardless calibration	Top of crack fill	5.96	4.23	0.54		0.06	0.22		0.14		0.18	14.74	101.85
Top2	Normal WROXI	Upper layer of subsoil	61.94	13.10	5.75	0.17	1.27	0.36	0.26	3.94	0.67	0.24	4.79	98.49
Top3	Normal WROXI	60mm below TOP2	82.37	6.34	2.59	0.10	0.32	0.22	0.30	2.08	0.42	0.18	2.86	98.30

Table 2: Bulk chemical analysis: minor and trace elements by XRF. < = below detection. All elements presented as wt% oxide.

	Calibration	**SO_3**	**V_2O_5**	**Cr_2O_3**	**SrO**	**ZrO2**	**BaO**	**NiO**	**CuO**	**ZnO**	**PbO**	**HfO2**
Top1	Normal WROXI	0.792	<0.007	0.016	0.012	<0.005	0.084	<0.006	0.034	0.003	97.300	0.106
Top1	Standardless calibration	0.417							0.057		75.320	
Top2	Normal WROXI	0.006	0.015	0.016	0.003	0.030	0.128	0.006	0.008	0.013	5.771	0.008
Top3	Normal WROXI	<0.003	0.007	0.010	<0.004	0.042	0.068	0.004	0.003	0.006	0.394	<0.004

Table 3. Bulk chemical analyses in wt% recast on a lead-free basis, with comparative data after Dunster & Dungworth (2012).

	SiO_2	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**Mn_3O_4**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**
St Algar's Farm	49.3		3.8	0.8		2.9	40.6		1.3	<1
Pentreheyling	38.8		12.6	0.5		2.8	43.6		3.1	<1
Top1	47.94	0.50	39.40	5.45	0.19	1.11	2.08	<	1.77	1.56
Top1	52.63	n.d.	37.31	4.79	n.d.	0.56	1.91	n.d.	1.21	1.60
Top2	70.63	0.77	14.94	6.56	0.20	1.45	0.41	0.29	4.49	0.28
Top3	86.78	0.44	6.68	2.73	0.11	0.34	0.23	0.31	2.19	0.19

Table 4. Bulk chemical analyses in wt% recast on a lead-free basis after removal of model bone ash content (model excipient methodology after Girbal 2011)

	SiO_2	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**Mn_3O_4**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**
Top1	49.73	0.52	40.86	5.66	0.20	1.15	0.06		1.83	
Top1	54.47		38.61	4.96		0.58			1.25	0.13
Top2	71.08	0.77	15.03	6.60	0.20	1.46	0.05	0.30	4.52	
Top3	87.14	0.44	6.71	2.74	0.11	0.34		0.32	2.20	0.01

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