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Summary

Eight fragments of "litharge cakes" excavated from Roman contexts were examined and analysed qualitatively by X-ray diffraction and X-ray fluorescence. The material was found to contain a number of lead compounds including litharge (lead monoxide) in hydrated form as well as traces of copper, silver and tin. It is likely that the material formed as a result of the cupellation of lead used to extract silver from a silver-containing copper alloy.

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ANALYSES OF SOME "LITHARGE CAKES" FROM SOUTHWARK CATHEDRAL, LONDON

Eight pieces of material excavated from Roman contexts under Southwark Cathedral crypt in 1977, and thought to be metallugical waste, were examined and analysed qualitatively by X-ray diffraction (XRD) and X-ray fluorescence (XRF). The pieces were generally plano-convex in form and varied in size, weighing between 70g and about 2.5kg. The bulk of the material was a buff colour, although patches were coloured green, and thin brown and black sooty layers were found on the underside (convex side) of some of the pieces. A number of the fragments had a dull grey coloured layer on the top side. Material of this type is usually refered to as "litharge cakes". Litharge is the term generally used to describe lead monoxide (PbO), although more properly the name refers specifically to the tetragonal allotrope.

XRD analyses of three of the samples showed that the bulk of the material was a combination of lead carbonate ($PbCO_3$), minium or red lead (Pb_3O_4), and the hydrated form of lead monoxide $3PbO.H_2O$.

XRF analyses were carried out in a number of areas on each of the pieces and significant levels of lead and copper were detected on all of them (as well as iron and manganese which probably originated mostly from soil contamination). Traces of silver and tin were also detected; silver being detected on six of the pieces and tin on seven. In each case silver was only detectable on the top surface of the cake, which was also where the highest levels of tin were noted. Although lead and copper levels remained fairly consistant throughout the analyses, tin and particularly silver levels were quite variable. This probably reflects the tendency of silver to collect into small droplets which, on close examination, could be seen as distict black "blobs" on the surfaces of several of the fragments.

Two pieces of fuel ash (alkali silicate) slag, one of which had a fragment of fired clay (possibly hearth lining) attached, were also examined and analysed by XRF. Significant levels of iron, as

well as slight traces of copper and lead, were detected. Although it is possible that the fuel ash slag may be related to the other material described it is non-diagnostic beyond indicating the presence of a fire at high temperature.

Litharge is a by-product of the cupellation process used to extract silver from lead. Cupellation involves the oxidation of lead to litharge by raising the lead to a temperature of about 1000-1100^{o}C in an oxidizing environment. This was usually achived by heating the lead in a shallow hearth, thereby exposing as much of the molten metal as possible to the air blast from the bellows. Any base metals present in the lead are dissolved in the litharge leaving any noble metals (silver and gold) which were present in the lead unaltered as a small "button". The shape of the hearth accounts for the characteristic plano-convex shape of the litharge cake which is left after cupellation.

The significant levels of copper and the traces of tin detected indicate that the litharge from this site did not originate as a result of the cupellation of newly smelted lead. However it is known that the cupellation process was also used as a method of extracting silver from copper/silver alloys (ie debased coinage or even silver-bearing copper smelted from argentiferous copper ores). One method of doing this is to cupel the copper/silver alloy along with the lead. The copper is then taken up in the litharge and the silver liberated. The process requires constant supervision since lead must be added at frequent intervals in order to make sure that all of the copper is removed.

Tylecote (1986,61) has speculated that another, more efficient, desilverizing process may have been used by the Romans. The technique, known as "lead soaking", involves melting the silver/copper alloy with lead. The silver dissolves preferentially in the lead which is then sepatated from the copper by virtue of its lower melting point. The silver, which is now dissolved in the lead, can then be extracted by simple cupellation rather than by cupelling the copper alloy and lead together.

The traces of tin detected in the litharge from this site suggest that the material being refined was not a copper/silver alloy smelted from an argentiferous copper ore as very few British copper ores contain significant levels of tin. It is notable however that much of the late Roman "bronze" coinage found in England contains small amounts of silver (Cope & Billingham 1967,1968a,1968b,1969a,1969b) which may have been added for economic reasons or to improve the apperance of the coins. It may be that the litharge cakes found on this site resulted from a process of extracting silver from material of this sort.

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