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Ancient silver embrittlement: significances of copper, lead and cold-deformation

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Ancient Silver Embrittlement: Significances of Copper, Lead, and Cold-Deformation

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Abstract

Mechanisms of corrosion-induced and microstructurally-induced embrittlement of ancient silver are concisely reviewed before making a statistical analysis of the copper and lead contents of objects containing at least 95 wt.% silver. This analysis, with information from studies on an Egyptian vase and the Gundestrup Cauldron, enables concluding that corrosion-induced embrittlement may be a widespread problem in high-purity ancient silver, with remanent cold-deformation being primarily responsible, though copper content will play a role. Also, studies of other embrittled objects will probably reveal more examples of microstructurally-induced embrittlement, which is thought to be due to lead segregation.

Keywords: ancient silver, chemical composition, corrosion, microstructure, grain boundaries, cracks, brittle fracture

Introduction

Ancient silver can be embrittled by long-term corrosion and microstructural changes (Thompson and Chatterjee 1954; Smith 1965; Werner 1965; Organ 1977; Kallfass *et al.* 1985; Ravich 1993; Wanhill *et al.* 1998; Wanhill 2002,2003a,2003b). The types of embrittlement have recently been discussed at length (Wanhill 2002,2003a,2003b) and hence will be summarised here.

Corrosion-induced embrittlement is due to several forms of selective corrosion: intergranular; interdendritic in essentially as-cast objects; along segregation bands; and along slip lines and deformation twin boundaries in objects containing remanent cold-deformation. All these forms of corrosion are due to local galvanic attack, whereby copper segregation has the primary role in intergranular, interdendritic and segregation band corrosion. Intergranular corrosion is partly a consequence of low-temperature segregation of copper that results in so-called discontinuous precipitation at grain boundaries. Interdendritic and segregation band corrosion are consequences of high-temperature segregation of copper during solidification of the molten silver alloy. Corrosion along slip lines and deformation twin boundaries is facilitated by locally high strains.

Microstructurally-induced embrittlement is characterized by brittle intergranular fracture, with sharply defined cracks and grain boundary facets. The embrittlement is most probably a consequence of long-term low-temperature ageing, whereby an impurity element, or elements, segregates to grain boundaries. The available evidence indicates lead to be the most likely perpetrator, though this has yet to be established directly. Other impurity elements might be involved, notably bismuth.

Synergistic embrittlement is due to the interaction of corrosion-induced and microstructurally-induced embrittlement. Corrosion along slip lines, deformation twin boundaries and segregation bands can resries. In turn, the grain boundary fractures expose more slip lines, deformation twins and segregation bands to the environment and increase the opportunities for corrosion.

In view of the foregoing information, the copper and lead contents and remanent cold-deformation should be primary factors in the embrittlement of ancient silver. However, opinions differ as to the extent and importance of embrittlement in ancient silver objects and the roles of copper and lead (Wanhill 2002). Also, the relative significances of all three factors have yet to be determined. The present work intends to shed some light on these issues.

Compositions of ancient silver

General remarks

Native silver alloys may or may not have been used for Old World ancient objects (Lucas 1928; Gale and Stos-Gale 1981a; Philip and Rehren 1996). However, the general scarcity of native silver compared to silver-containing minerals, mostly lead ores, and the early development of lead cupellation, resulted on pyrometallurgy becoming the main source of silver (Gowland 1918; Gale and Stos-Gale 1981a,1981b; Tylecote 1986; Raub 1995).

Cupellation is very effective in producing silver above 95 wt.% purity (Tylecote 1986,1987), though it usually contains minor-to-trace amounts of gold, copper, lead and bismuth, and traces of antimony, arsenic, tellurium, zinc and nickel (McKerrell and Stevenson 1972; Gale and Stos-Gale 1981a; Raub 1995). Gold, copper, lead and bismuth contents are generally below 1 wt.% for each element.

Cupellation experiments by McKerrell and Stevenson (1972) showed that copper was readily reduced to the 0.2 - 0.5 wt.% level, with lead and bismuth typically remaining at the 0.5 - 1 wt.% level. However, Gale and Stos-Gale (1981a) interpret the copper and lead contents more broadly: copper up to 1 wt.% and lead from 0.05 - 2.5 wt.%. From these authorities it appears that copper contents above 0.5 - 1 wt.% would indicate deliberate additions, probably to increase the strength and wear resistance. Remarkably, this practice seems to have been followed from very early times (Gale and Stos-Gale 1981a), as far back as 3000 BCE.

Copper and lead in objects at least 95 wt.% silver: statistics

Tables 1 and 2 give copper and lead percentages for many Old World artefacts and coins containing at least 95 wt.% silver. The data are from Lucas (1928), Elam (1931), Caley (1964), Hawkes *et al.* (1966), Cope (1972), MacDowall (1972), McKerrell and Stevenson (1972), Müller and Gentner (1979), Gale and Stos-Gale (1981a), Bennett (1994), Perea and Rovira (1995), Wanhill *et al.* (1998), and Northover (2003).

Figure 1 shows histograms of the data. Figure 1a shows the copper percentages approximate to a normal distribution except for a high "tail" in the range 0 - 0.5 wt.% copper. Figures 1b and 1c show that the lead percentages appear almost log-normally distributed, with a positive skew in the middle ranges.

Figures 2 and 3 present the ordered (median ranked) data on probability plots. Figure 2 shows that the cumulative occurrence of copper percentages fits a normal distribution, apart from the "tails". The normal distribution (including the "tails") was confirmed by the χ^2 test for goodness of fit, dividing the data into four intervals on the basis of a normal distribution, and choosing a significance level of 5%. The arrows in table 1 specify the data within the intervals.

Figure 3 shows that the cumulative occurrence of lead percentages *appears* to follow a log-normal distribution. The χ^2 test for goodness of fit was applied by dividing the data into four intervals on the basis of a log-normal distribution, and choosing a significance level of 5%. The χ^2 test showed that the distribution was not log-normal, since there were too many data in the third interval, see table 2, in the range 0.4 - 0.7 wt.% lead. This range corresponds to the positive skew in figure 1c.

Interpretation of the statistical results

There is no intrinsic reason why any set of data should be described perfectly by simple mathematical distributions like the normal and log-normal distributions. However, when *adequate* descriptions are obtained, the statistical results can be most useful.

In the first instance, the data in figures 2 and 3 show a high degree of homogeneity, even though taken from a wide variety of sources. This is most probably because cupellation was the main source of the silver. Secondly, since the copper percentages are normally distributed, this implies that any additions of copper to improve the strength and wear resistance were unsystematic for objects containing at least 95 wt.% silver. Thirdly, although the lead percentages did not satisfy the χ^2 test for goodness of fit to a log-normal distribution, the straight line fit in figure 3 is adequate. The practical significance of this admittedly subjective judgement is that a log-normal (or approximately log-normal) distribution can be applied to the concentrations of chemical process residues (Lipson and Sheth 1973). In other words, the fair correlation in figure 3 suggests that the lead percentages came from the residual lead contents after cupellation.

Examples of ancient silver embrittlement and compositions

Figures 2 and 3 include data points for two ancient silver artefacts, an Egyptian vase (300 - 200 BCE) and the famous Gundestrup Cauldron (200 - 100 BCE). Embrittlement of the Egyptian vase was investigated by Wanhill *et al.* (1998). Embrittlement of samples from the Gundestrup Cauldron was recently studied in a collaborative project between Oxford University and the NLR (Wanhill *et al.* 2003).

The Egyptian vase had undergone both corrosion-induced and microstructurally-induced embrittlement. The corrosion-induced embrittlement was primarily along slip lines and deformation twin boundaries owing to remanent cold-deformation. The copper content was only 0.9 wt.%, and there was no evidence of discontinuous precipitation. The lead content was 0.7 wt.%, but no bismuth was detected.

The Gundestrup Cauldron samples 363 and 365 had undergone corrosion-induced embrittlement owing to remanent cold-deformation. The cracks were mainly at grain boundaries but also along slip lines and deformation twin boundaries. There was no evidence of discontinuous precipitation. Sample 363 contained 1.76 wt.% copper and 0.52 wt.% lead; sample 365 contained 2.17 wt.% copper and 0.58 wt.% lead.
In contrast, the Gundestrup Cauldron sample 366 was essentially in the annealed condition, free of corrosion, and unembrittled. There was, however, extensive discontinuous precipitation of copper at the grain boundaries. The copper and lead contents were 3.44 wt.% and 0.64 wt.% respectively.

Discussion

Background

Opinions differ as to the seriousness of silver embrittlement. Schweizer and Meyers (1979) and Kallfass *et al.* (1985) aver that ancient silver is often extremely brittle. On the other hand, Northover (1999) has examined hundreds of artefacts and coins, finding only a small proportion to be badly embrittled. On neutral ground, Thompson and Chatterjee (1954) and Werner (1965) state that it is well known that certain silver objects have become very brittle.

The role of copper, specifically the copper content, is also debatable. Smith (1965) stated that ancient silver with more than about 3 % copper is invariably brittle. However, Northover (1999) found that intergranular corrosion and cracking were most prevalent at low copper contents, for example in ancient Bactrian silver, which often contains less than 1 % copper.

Corrosion-induced embrittlement

The observations on corrosion-induced embrittlement of the Egyptian vase and the Gundestrup Cauldron show that it occurs at copper contents less than 1 wt.%, as Northover (1999) stated, that discontinuous precipitation of copper is not necessary, and that copper contents above 3 wt.% do not invariably mean embrittlement. Instead it appears that remanent cold-deformation is of primary importance.

Returning to figure 2, we see that for objects containing at least 95 wt.% silver, about half will have copper contents less than 2 wt.%. For sufficient strength in everyday use, many of these objects would contain remanent cold-deformation, as did the Egyptian vase (Wanhill *et al.* 1998). In other words, corrosion-induced embrittlement could be a widespread problem in high-purity ancient silver. There are, of course, additional factors to consider, including an object's burial time and the average temperature, moisture content, pH and chemical composition of the burial environment, especially the salt, nitrate and nitrite contents (Gowland 1918).

Microstructurally-induced embrittlement

Mechanical testing of age-hardened silver-lead and silver-lead-copper alloys (Thompson and Chatterjee 1954) and observations on the Egyptian vase (Wanhill *et al.* 1998) indicate that 0.7-0.8 wt.% lead is sufficient to embrittle silver. Additional experiments by Thompson and Chatterjee (1954) showed that lead could precipitate from supersaturated solid solution in silver at lead contents as low as 0.1 wt.%, thereby possibly causing embrittlement.

At present there is very limited published evidence of microstructurally-induced embrittlement of ancient silver (Thompson and Chatterjee 1954; Wanhill *et al.* 1998). Even so, figure 3 shows that for objects containing at least 95 wt.% silver, about a quarter will have lead contents more than 0.7 wt.%. This is a significant fraction, so detailed examination of other embrittled objects should reveal further instances of microstructurally-induced embrittlement. However, see the next subsection, synergistic embrittlement.

Synergistic embrittlement

Corrosion-induced embrittlement is more in evidence than microstructurally-induced embrittlement, and is probably much more widespread. Thus it seems also more probable that synergistic embrittlement would occur rather than microstructurally-induced embrittlement on its own.

Conclusions

Evidence of corrosion-induced and microstructurally-induced embrittlement of ancient silver, and a statistical treatment of the copper and lead contents of objects containing at least 95 wt.% silver, indicate the following:

(1) Corrosion-induced embrittlement may be a widespread problem in high-purity ancient silver.

(2) Remanent cold-deformation is of primary importance in causing corrosion-induced embrittlement, though copper content will also play a role.

(3) Detailed examination of other embrittled objects is likely to reveal further examples of synergistic embrittlement. This occurs by the interaction of corrosion-induced and microstructurally-induced embrittlement, which is probably due to lead.

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Table 1 Ranked copper contents of ancient silver artefacts and coins containing at least 95 wt.% silver

Cu wt.%	**median rank (%)**	**Cu wt.%**	**median rank (%)**	**Cu wt.%**	**median rank (%)**	**Cu wt.%**	**median rank (%)**	**Cu wt.%**	**median rank (%)**
0.02	0.48	0.98	21.0	1.90	40.8	2.40	62.0	3.11	82.4
0.04	1.16	1.00	21.7	1.97	42.1	2.43	62.6	3.20	83.1
0.05	1.84	1.00	21.7	2.00	42.8	2.49	63.3	3.26	83.8
0.07	2.53	1.00	21.7	2.00	42.8	2.50	64.0	3.30	84.5
0.08	3.21	1.00	21.7	2.00	42.8	2.50	64.0	3.30	84.5
0.10	3.89	1.07	24.4	2.00	42.8	2.58	65.4	3.30	84.5
0.15	4.58	1.17	25.1	2.00	42.8	2.58	65.4	3.40	86.5
0.19	5.26	1.20	25.8	2.00	42.8	2.63	66.7	3.40	86.5
0.22	5.94	1.20	25.8	2.00	42.8	2.67	67.4	3.40	86.5
0.23	6.63	1.26 ←	27.1	2.00	42.8	2.70	68.1	3.44	88.6
0.23	6.63	1.31	27.8	2.00	42.8	2.70	68.1	3.50	89.3
0.23	6.63	1.33	28.5	2.00	42.8	2.76	69.5	3.54	90.0
0.24	8.67	1.34	29.2	2.02 ←	49.7	2.78 ←	70.2	3.60	90.6
0.24	8.67	1.40	29.8	2.07	50.3	2.80	70.8	3.61	91.3
0.29	10.0	1.42	30.5	2.10	51.0	2.80	70.8	3.62	92.0
0.41	10.7	1.42	30.5	2.10	51.0	2.81	72.2	3.70	92.7
0.50	11.4	1.50	31.9	2.10	51.0	2.90	72.9	3.70	92.7
0.51	12.1	1.61	32.6	2.15	53.1	2.95	73.6	3.71	94.1
0.58	12.8	1.64	33.3	2.17	53.8	3.00	74.2	3.80	94.7
0.60	13.5	1.70	33.9	2.20	54.4	3.00	74.2	3.81	95.4
0.72	14.1	1.70	33.9	2.20	54.4	3.00	74.2	3.82	96.1
0.73	14.8	1.70	33.9	2.20	54.4	3.00	74.2	3.86	96.8
0.80	15.5	1.71	36.0	2.20	54.4	3.00	74.2	3.90	97.5
0.80	15.5	1.73	36.7	2.24	57.2	3.00	74.2	4.01	98.2
0.81	16.9	1.75	37.4	2.25	57.9	3.00	74.2	4.30	98.8
0.83	17.6	1.76	38.0	2.26	58.5	3.00	74.2	4.33	99.5
0.84	18.2	1.77	38.7	2.30	59.2	3.00	74.2		
0.85	18.9	1.80	39.4	2.30	59.2	3.06	80.4		
0.90	19.6	1.85	40.1	2.31	60.6	3.10	81.1		
0.95	20.3	1.90	40.8	2.34	61.3	3.10	81.1		

Table 2 Ranked lead contents of ancient silver artefacts and coins containing at least 95 wt.% silver

Pb		median rank (%)	Pb		median rank (%)	Pb		median rank (%)	Pb		median rank (%)
wt.%	log wt.%		wt.%	log wt.%		wt.%	log wt.%		wt.%	log wt.%	
0.036	-1.44	0.56	0.22	-0.658	24.7	0.45	-0.347	50.4	0.70	-0.155	73.7
0.041	-1.39	1.36	0.22	-0.658	24.7	0.45	-0.347	50.4	0.70	-0.155	73.7
0.05	-1.30	2.17	0.22	-0.658	24.7	0.46	-0.337	52.0	0.70	-0.155	73.7
0.051	-1.29	2.97	0.25	-0.602	27.9	0.46	-0.337	52.0	0.70	-0.155	73.7
0.051	-1.29	2.97	0.25	-0.602	27.9	0.46	-0.337	52.0	0.72	-0.143 ←	78.5
0.06	-1.22	4.58	0.25	-0.602	27.9	0.46	-0.337	52.0	0.81	-0.092	79.3
0.066	-1.18	5.39	0.26	-0.585	30.3	0.46	-0.337	52.0	0.84	-0.076	80.1
0.068	-1.17	6.19	0.26	-0.585	30.3	0.46	-0.337	52.0	0.85	-0.071	80.9
0.10	-1	6.99	0.29	-0.538	31.9	0.50	-0.301	56.8	0.86	-0.066	81.8
0.10	-1	6.99	0.30	-0.523	32.7	0.50	-0.301	56.8	0.86	-0.066	81.8
0.10	-1	6.99	0.30	-0.523	32.7	0.50	-0.301	56.8	0.90	-0.046	83.4
0.10	-1	6.99	0.30	-0.523	32.7	0.50	-0.301	56.8	0.90	-0.046	83.4
0.10	-1	6.99	0.30	-0.523	32.7	0.50	-0.301	56.8	0.90	-0.046	83.4
0.13	-0.886	11.0	0.30	-0.523	32.7	0.52	-0.284	60.9	0.92	-0.036	85.8
0.13	-0.886	11.0	0.30	-0.523	32.7	0.53	-0.276	61.7	0.97	-0.013	86.6
0.14	-0.850	12.6	0.36	-0.444	37.5	0.56	-0.252	62.5	1.00	0	87.4
0.14	-0.850	12.6	0.39	-0.409	38.3	0.57	-0.244	63.3	1.00	0	87.4
0.16	-0.796	14.2	0.39	-0.409 ←	38.3	0.58	-0.237	64.1	1.02	0.009	89.0
0.16	-0.796	14.2	0.40	-0.398	40.0	0.58	-0.237	64.1	1.03	0.013	89.8
0.16	-0.796	14.2	0.40	-0.398	40.0	0.58	-0.237	64.1	1.08	0.033	90.6
0.18	-0.744	16.6	0.40	-0.398	40.0	0.60	-0.222	66.5	1.10	0.041	91.4
0.20	-0.699	17.4	0.41	-0.387	42.4	0.60	-0.222	66.5	1.10	0.041	91.4
0.20	-0.699	17.4	0.42	-0.377	43.2	0.60	-0.222	66.5	1.17	0.068	93.0
0.20	-0.699	17.4	0.42	-0.377	43.2	0.60	-0.222	66.5	1.27	0.104	93.8
0.20	-0.699	17.4	0.42	-0.377	43.2	0.60	-0.222	66.5	1.36	0.134	94.6
0.20	-0.699	17.4	0.43	-0.367	45.6	0.63	-0.201	70.5	1.49	0.173	95.4
0.20	-0.699	17.4	0.43	-0.367	45.6	0.63	-0.201	70.5	2.19	0.340	96.2
0.20	-0.699	17.4	0.43	-0.367	45.6	0.64	-0.194	72.1	2.70	0.431	97.0
0.20	-0.699	17.4	0.44	-0.357	48.0	0.68	-0.167	72.9	2.87	0.458	97.8
0.20	-0.699 ←	17.4	0.44	-0.357	48.0	0.70	-0.155	73.7	3.05	0.484	98.6
0.22	-0.658	24.7	0.44	-0.357	48.0	0.70	-0.155	73.7	3.68	0.566	99.4

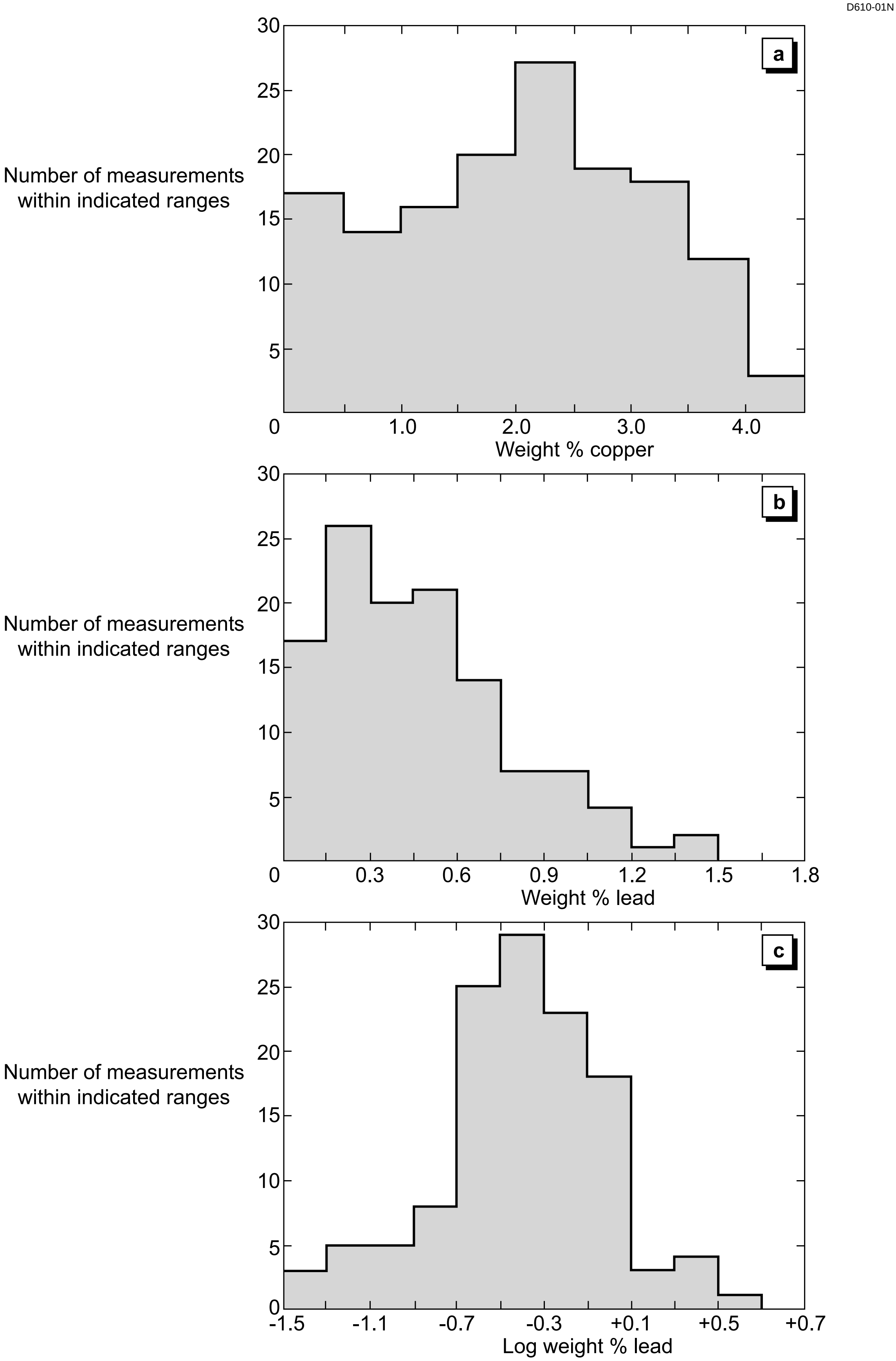

Fig. 1 Histograms of the copper and lead contents in ancient artefacts and coins containing at least 95 wt. % silver: data from tables 1 and 2

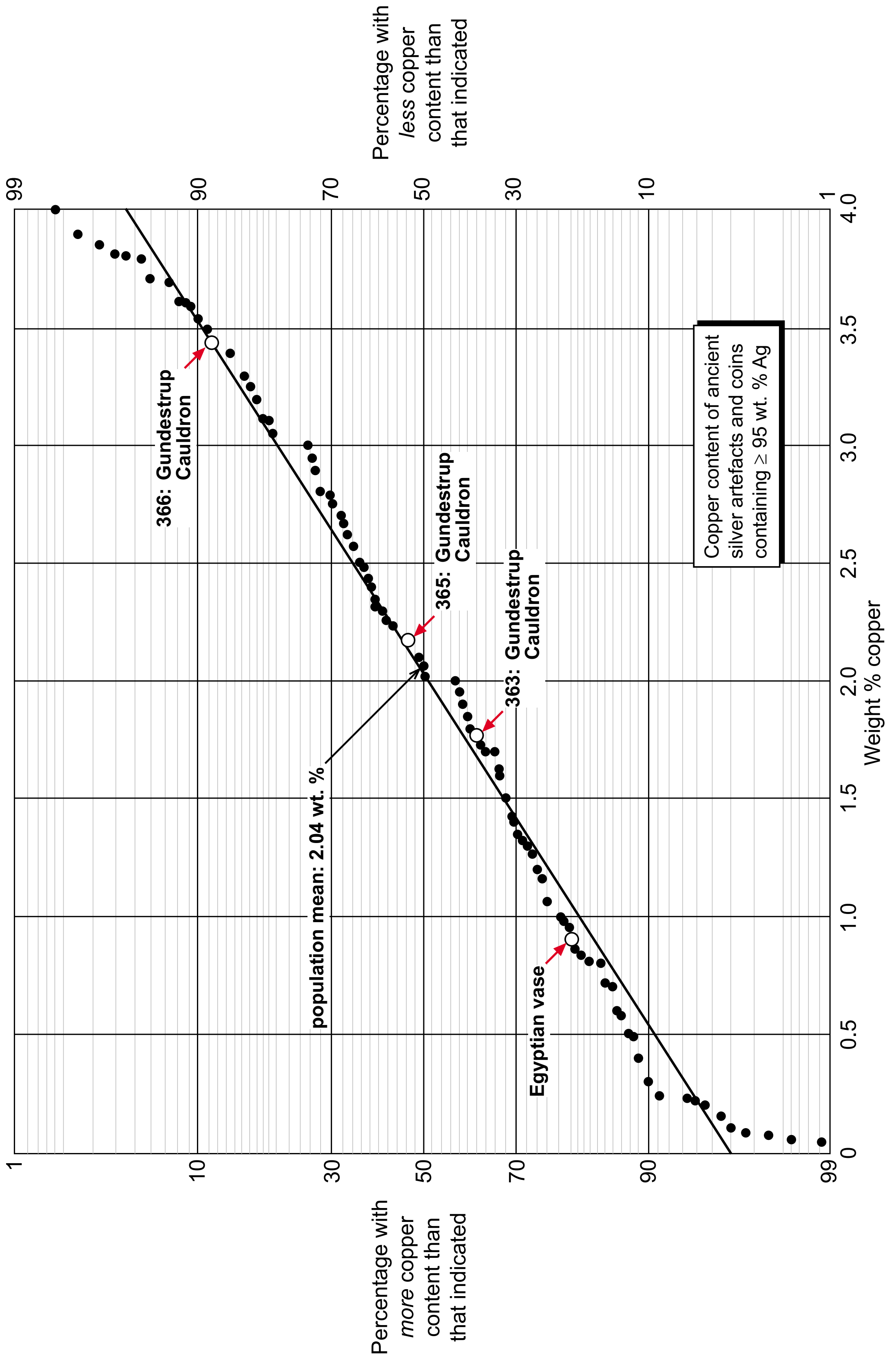

Fig. 2 Normal probability plot of copper contents in ancient artefacts and coins containing at least 95 wt. % silver: data from table 1

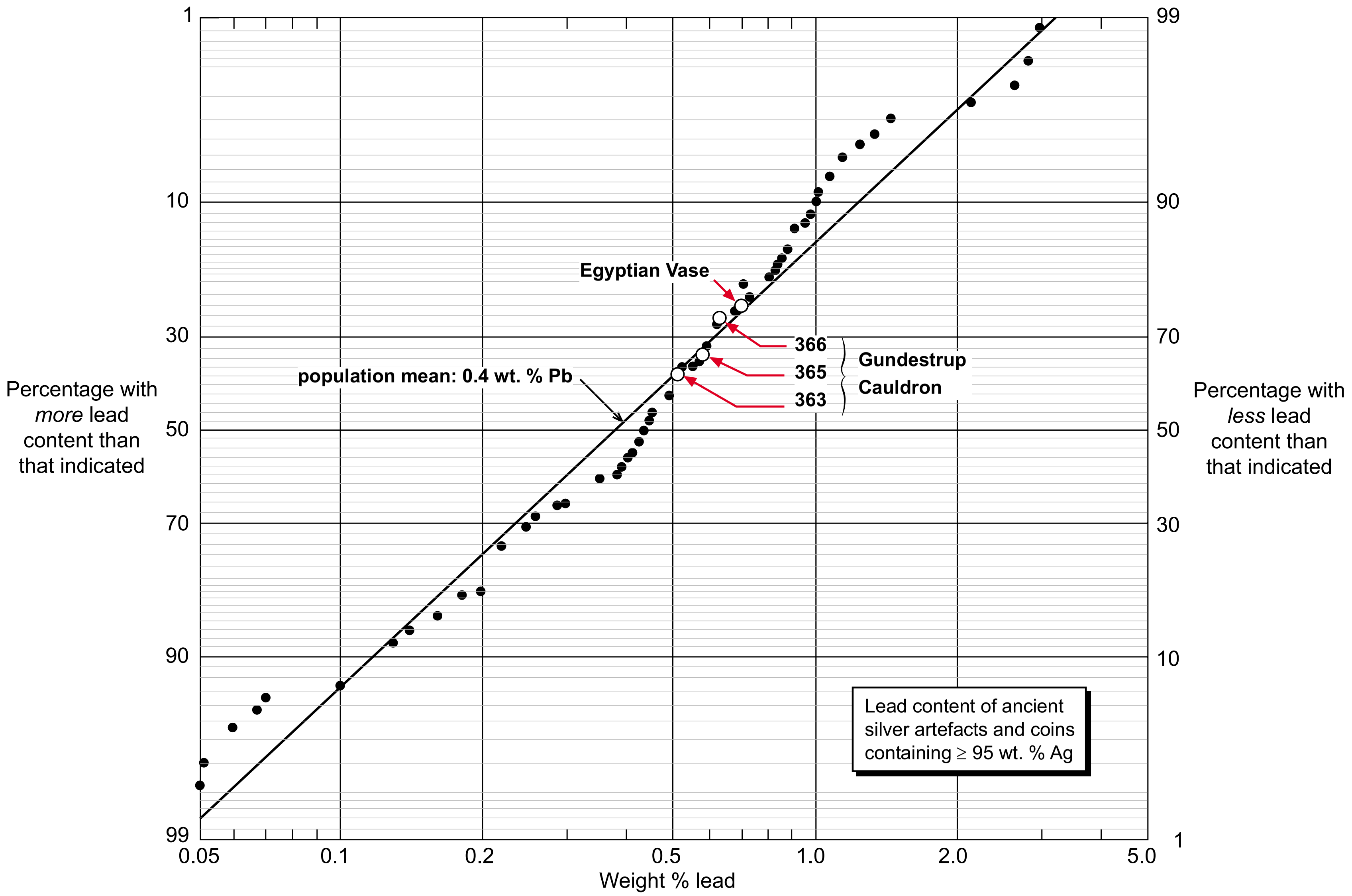

Fig. 3 Log normal probability plot of lead contents in ancient artefacts and coins containing at least 95 wt. % silver: data from table 2