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ABSTRACT

Discontinuous precipitation of copper has been held responsible for much of the embrittlement of ancient silver objects, and its detailed characteristics have been suggested as possible indicators of an object's authenticity. These possibilities were checked by studying samples from the Gundestrup Cauldron, using electron backscatter diffraction (EBSD) with scanning electron microscopy (SEM). The results indicate that discontinuous precipitation is much less significant for embrittlement than remanent deformation from final mechanical working, and that the precipitation characteristics cannot be used for authentication. It is recommended to broaden the database for embrittled objects with the aid of modern and versatile analysis techniques like EBSD + SEM.

Nationaal Lucht- en Ruimtevaartlaboratorium
National Aerospace Laboratory NLR

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On the Significance of Discontinuous Precipitation of Copper in Ancient Silver

R.J.H. Wanhill[1], J.P. Northover[2] and T. Hattenberg[1]

Abstract

Discontinuous precipitation of copper has been held responsible for much of the embrittlement of ancient silver objects, and its detailed characteristics have been suggested as possible indicators of an object's authenticity. These possibilities were checked by studying samples from the Gundestrup Cauldron, using electron backscatter diffraction (EBSD) with scanning electron microscopy (SEM). The results indicate that discontinuous precipitation is much less significant for embrittlement than remanent deformation from final mechanical working, and that the precipitation characteristics cannot be used for authentication. It is recommended to broaden the database for embrittled objects with the aid of modern and versatile analysis techniques like EBSD + SEM.

Keywords: ancient silver, silver-copper alloys, corrosion, cracks, grain boundaries, electron backscatter diffraction, scanning electron microscopy, microstructure

Introduction

Discontinuous precipitation of copper in ancient silver has been held responsible for corrosion-induced and microstructurally-induced embrittlement (Smith 1965; Werner 1965). The eminent metallurgist C.S.Smith also stated that "silver alloys of any antiquity containing over about three percent copper are invariably brittle" (Smith 1965). By this he apparently meant - the text is not entirely clear - that the brittleness was due mainly to corrosion along grain boundaries where discontinuous precipitation had occurred.

The idea that copper precipitation could result in microstructurally-induced embrittlement was proposed by Werner (1965). This was taken up by Schweizer and Meyers (1978a, 1978b, 1979), who suggested also that the widths and detailed morphology of discontinuous precipitation might enable verification of the age, and hence authenticity, of silver artefacts.

The present work considers discontinuous precipitation of copper in ancient silver in the light of the foregoing assertions and suggestions. First, we review briefly the metallurgical literature on discontinuous precipitation of copper in silver. There follows a survey of its relevance to corrosion-induced and microstructurally-induced embrittlement of ancient silver. Then the overall significance of discontinuous precipitation for ancient silver will be addressed using

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the preceding survey, additional information from the literature, and new results from samples of the Gundestrup Cauldron, a masterpiece of European Iron Age silverwork.

Discontinuous precipitation of copper in silver

Basic characteristics of discontinuous precipitation

Discontinuous precipitation is growth of a two-phase product behind a moving grain boundary that relieves a supersaturated α matrix, the reaction being $\alpha \rightarrow \alpha' + \beta$, see figure 1. The adjective "discontinuous" refers to an abrupt change in matrix composition ($\alpha : \alpha'$) and not to the precipitate morphology.

The reaction begins with nucleation of β at the grain boundary. As it moves, the grain boundary collects solute from the supersaturated α matrix, and the precipitate phase β is then supplied with solute by grain-boundary diffusion, which is much faster than solute diffusion in the matrix. The result is that the β precipitates can grow while remaining attached to the moving grain boundary. In turn, this often results in a lamellar microstructure behind the grain boundary, as indicated in figure 1. This figure also shows schematically, via colour-shading, that the depleted matrix, α', in the precipitation zone has changed its crystallographic orientation from that of grain 2 to that of grain 1. This is an essential characteristic of discontinuous precipitation (Gust 1979).

Copper in silver

Discontinuous precipitation of copper in silver-copper alloys was first investigated by Fraenkel (1926). Many studies followed, e.g. Norbury (1928), Ageew *et al.* (1930), Barrett *et al.* (1935), Cohen (1937), Jones *et al.* (1942), Gayler and Carrington (1947), Rose (1957), Leo (1967), Predel and Ruge (1968), Scharfenberger *et al.* (1972), Gust *et al.* (1978), Pawlowski (1979a, 1979b). All of these studies involved precipitation experiments (ageing) at elevated temperatures, usually above 200 ºC.

Figure 2 illustrates the development of discontinuous precipitation in standard silver (Norbury 1928). There are several noteworthy features, visible also in other studies (Cohen 1937; Gayler and Carrington 1947; Rose 1957; Smith 1965; Leo 1967; Predel and Ruge 1968; Scharfenberger *et al.* 1972; Schweizer and Meyers 1978a, 1979):

(1) The precipitate colonies can be very variable in size, figures 2b, 2c, and their appearance is finely-mottled, not lamellar. A lamellar microstructure often does not occur, especially at lower ageing temperatures (Gayler and Carrington 1947).

(2) Colonies can grow in opposite directions from adjacent or overlapping sites on the same original grain boundary. This occurs in other alloys too (Williams and Edington 1976). In view of the precipitation mechanism, this phenomenon is difficult to explain (Doherty 1996).

(3) Although the original grain boundaries are slightly curved or straight, the new grain boundaries formed by the moving reaction fronts are irregular. At low magnifications this irregularity gives the new grain boundaries a meandering, wiggly appearance (Smith 1965).

Figure 3 is a compilation of discontinuous precipitate growth rates versus ageing temperatures for modern silver-copper alloys annealed before ageing. The ordinate and abscissa scales assume Arrhenius reaction kinetics that enable straight-line extrapolations of the data to lower ageing temperatures. These extrapolations suggest a maximum growth rate of 10^{-3} μm/year at ambient temperatures. For artefacts 1000-2000 years old this means maximum precipitate widths of 1-2 μm. These would be visible from metallography, but there are two caveats. First, the extrapolations ask much of the available data. Figure 3 shows that it is a long way from precipitation at 200 ºC to possible precipitation at ambient temperatures, and there is no guarantee that Arrhenius reaction kinetics apply over the whole range. Second, elevated temperature tests demonstrated incubation times before precipitation began (Gust *et al*. 1978). At ambient temperatures the incubation times could be very long, centuries or even millenia.

Be that as it may, some ancient silver shows what is reasonably assumed to be discontinuous precipitation of copper (Smith 1965; Schweizer and Meyers 1978a, 1979; Wanhill 2002), and it might have occurred mainly at ambient temperatures.

Corrosion-induced embrittlement

Corrosion types

Several types of corrosion can embrittle ancient silver. In high-silver-content alloys general corrosion slowly converts the metal surface to silver chloride (Gowland 1918; Organ 1977; Scott 1996). The silver chloride forms a brittle, finely granular layer but does not affect the remaining metal.

The other types of corrosion are selective, penetrating the metal and reducing its resistance to cracking (Werner 1965; Ravich 1993; Wanhill *et al*. 1998). Intergranular corrosion is the most commonly reported type, and occurs in mechanically worked and annealed artefacts, which constitute the majority. Interdendritic corrosion can occur in castings or essentially as-cast artefacts (Scott 1996), but these are rare.

Transcrystalline corrosion, along slip lines and deformation twin boundaries, can occur in objects not annealed after final mechanical working, which includes general deformation as in striking a coin (Thompson and Chatterjee 1954) and local deformation owing to decorating by chasing and stamping (Wanhill *et al*. 1998). Inside the metal these types of corrosion facilitate additional corrosion along segregation bands, if present (Wanhill *et al*. 1998). These bands are the remains, modified by mechanical working and annealing, of solute element segregation (coring) and interdendritic segregation that occurred during metal solidification.

Corrosion mechanisms

Intergranular corrosion is attributed, at least partly, to low temperature segregation of copper - specifically discontinuous precipitation - along the grain boundaries (Smith 1965; Werner 1965; Ravich 1993). Interdendritic and segregation band corrosion are also due to copper segregation, which in these cases occurred at high temperatures. The actual mechanism of all these types of corrosion is localised galvanic attack, whereby the more noble silver matrix acts as cathode and the copper-enriched regions dissolve anodically.

Corrosion along slip lines and deformation twin boundaries is due to locally high strains and the possibility of long-term segregation of solute or impurity elements to the highly strained regions. The resulting cracks are crystallographic and faceted (Wanhill *et al*. 1998) and may be a kind of stress corrosion cracking (Wanhill 2002).

Microstructurally-induced embrittlement

Microstructurally-induced embrittlement of ancient silver is intergranular (Wanhill *et al*. 1998). The intergranular cracks are characteristically narrow and sharp except where grains become bodily displaced, which is itself a characteristic of severe embrittlement.

There have been three suggestions for the cause of microstructurally-induced embrittlement. These are lead precipitation at grain boundaries (Thompson and Chatterjee 1954), atomic segregation of lead to grain boundaries (Wanhill *et al*. 1998), and discontinuous precipitation of copper along grain boundaries (Werner 1965; Schweizer and Meyers 1978a).

Empirical evidence and modern concepts of embrittlement implicate lead and discount copper as the source of microstructurally-induced embrittlement (Thompson and Chatterjee 1954; Wanhill *et al*. 1998; Wanhill 2002). The best evidence against copper, obtained for other purposes, is provided by Norbury (1928). Figure 4 shows Norbury's mechanical property data for standard silver aged to contain increasing amounts of discontinuous precipitation of copper. Although there were large changes in tensile strength and elongation, the minimum tensile elongation was about 34%, which still indicates high ductility and certainly not embrittlement.

Significance of discontinuous precipitation in ancient silver

From the previous sections of this paper there are two main issues regarding discontinuous precipitation of copper in ancient silver. A third, more general, issue comes from the literature. These issues are presented next, followed by new findings from samples of the Gundestrup Cauldron. The findings contribute to all three issues, as will be discussed.

Main issues

(1) The preceding discussions of embrittlement types and mechanisms indicate that discontinuous precipitation of copper in ancient silver can be responsible for some of the corrosion-induced embrittlement, in the form of intergranular corrosion and cracking. Though important, this is less inclusive than the impressions given in the papers by Smith (1965) and Werner (1965). The issue is whether it is possible to be more specific.

(2) The proposal by Schweizer and Meyers (1978a, 1978b, 1979) that silver artefacts could be authenticated by the characteristics of discontinuous precipitation seems to have been abandoned. This proposal concerned two aspects, the precipitate width and its detailed morphology. This latter aspect can be dealt with immediately. Schweizer and Meyers (1979) suggested that the precipitate might form regular lamellae, whose spacing would depend on the ageing temperature such that one could distinguish between genuine long-term precipitation at ambient temperatures and short-term precipitation at elevated temperatures. However, all the evidence, exemplified by figure 2 and including the samples examined by Schweizer and Meyers (1978a, 1979), shows that the precipitate is finely-mottled, not lamellar.

(3) 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, one of us (JPN) 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 issue of copper content can be placed in this situation of uncertainty. Smith (1965) stated that ancient silver with more than about 3% copper is invariably brittle, and Gale and Stos-Gale (1981) found that 37% of many analysed silver artefacts contained more than 6% copper. This statement and information are compatible only with the opinion that ancient silver is often brittle. However, our experience (JPN) is that intergranular corrosion and cracking are most prevalent at low copper contents, for example in ancient Bactrian silver, which often contains less than 1% copper.

Gundestrup Cauldron samples

Automated electron backscatter diffraction (EBSD) was used with a field emission gun scanning electron microscope (FEG-SEM) to analyse four samples from different parts of the Gundestrup Cauldron, which dates to the 2nd or 1st century BCE. Figure 5 illustrates the Cauldron, which consists of twelve plates and a bowl, all of 94-98% silver. The samples had the following chemical compositions:

Sample	Cu	Au	Pb	Bi	Traces
361	4.64	0.29	0.39	0.07	Fe,Ni
363	1.76	0.35	0.52	0.13	Fe,Zn
365	2.17	0.33	0.58	0.11	Fe,Ni,Zn
366	3.44	0.36	0.64	0.11	Fe,Ni,Zn

Apart from the copper contents, the samples had fairly similar amounts of other elements, making them useful for archaeometallurgical studies.

After polishing, and etching with ammoniacal hydrogen peroxide, the samples were imaged by EBSD and FEG-SEM. Figures 6-10 and table 1 illustrate and summarise the findings in the order of increasing remanent deformation within the samples. In addition, the main results are described here:

(1) Sample 366 (figures 6,7). This sample was essentially annealed and virtually free of corrosion. There was extensive grain boundary precipitation of copper, and the details given in figure 7 prove it to be discontinuous precipitation. The precipitate was non-lamellar, and some widths were up to 7μm. This is well beyond the maximum of 2μm that is predictable from figure 3 for 2000 years of precipitation at ambient temperatures.

(2) Samples 361,363,365 (figures 8-10). These samples contained increasing amounts of remanent deformation and corrosion damage, visible as cracks. The cracks were mainly at grain boundaries, but were also transcrystalline, as best seen in figure 10a. However, there was no evidence of grain boundary precipitation.

The differences between sample 366 and samples 361, 363 and 365, with respect to remanent deformation, discontinuous precipitation and corrosion damage, are very significant. The link between remanent deformation and corrosion damage was noted earlier (Wanhill *et al*. 1998), and is reinforced by the results for samples 361, 363 and 365. Also, there is a possible, or probable, link between remanent deformation and discontinuous precipitation. Experiments have shown that cold-deformation can reduce the early growth rate, and hence width, of discontinuous precipitation in silver-copper alloys at elevated temperatures, and this could be due to deformation-induced continuous precipitation within the grains (Scharfenberger *et al*. 1972). A similar effect might have occurred in samples 361, 363, and 365, even to the extent that discontinuous precipitation was prevented. Finally, sample 366 demonstrates that the causality between discontinuous precipitation, copper content (above 3%) and corrosion damage is less certain than stated by Smith (1965).

Discussion of the main issues

The Gundestrup Cauldron sample analyses contribute to all three main issues concerning the significance of discontinuous precipitation in ancient silver, as follows:

(1) Even extensive discontinuous precipitation, in an alloy containing more than 3% copper, need not result in intergranular corrosion and cracking. On the other hand, remanent deformation from final mechanical working is highly detrimental.
The relative importance of remanent deformation, if present in an object, is emphasized by its apparent suppression or inhibition of discontinuous precipitation. Note that sample 361, containing the least remanent deformation, showed no evidence of discontinuous precipitation even though its copper content (4.64%) was higher than that of sample 366 (3.44%).

(2) The sample 366 precipitate widths, and the generally observed finely-mottled appearance of discontinuous precipitation of copper, exclude using the precipitate characteristics to determine the age and authenticity of silver artefacts.

(3) Figure 11 is a probability plot of copper content in ancient silver of at least 95% purity. The data follow a normal distribution. Since copper is readily reduced by cupellation to below 0.5% (McKerrell and Stevenson 1972), the data indicate - within the limits of 95-100% silver - that most of the objects contained unsystematic additions of copper.
Three of the Gundestrup Cauldron samples and a previously investigated Egyptian vase (Wanhill *et al*. 1998) are indicated in figure 11. Samples 363 and 365 and the vase contained remanent deformation and associated corrosion-induced cracking, while sample 366 was essentially annealed and free of corrosion-induced cracking. Thus an increasing copper content, even above the 3% stated by Smith (1965), does not simply correlate with increased susceptibility to corrosion-induced embrittlement.(This is probably just as well, since 80% of the objects plotted in figure 11 had copper contents higher than that of the Egyptian vase.)

Conclusions and recommendations

(1) Although discontinuous precipitation of copper in ancient silver can result in corrosion-induced intergranular cracking and embrittlement, its overall significance is likely to be much less than the embrittling influence of remanent deformation from final mechanical working of an object. Nor does increasing copper content, which would favour discontinuous precipitation, simply correlate with increased susceptibility to corrosion-induced embrittlement.

(2) The characteristics of discontinuous precipitation cannot be used to determine the age and authenticity of silver artefacts.

(3) Though giving explicit results, the present work relies on detailed microstructural analyses of samples from two ancient silver artefacts, the Gundestrup Cauldron and a previously studied Egyptian vase. The database needs broadening by detailed microstructural studies of other embrittled silver objects. In this respect the combination of EBSD and FEG-SEM is a powerful and versatile analysis technique.

(4) Conservators should pay particular attention to the condition of ancient silver objects known, or suspected, to contain remanent deformation.

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Table 1 EBSD analyses of Gundestrup Cauldron samples

Samples	Analysis types	Figures	Observations and interpretations
366	IPF colour coded map	6a	• random orientation equiaxed grains containing annealing twins; "black" ledges due to selective etching at precipitate boundaries
	Boundary rotation angle map	6b	• mainly 45º - 60º boundaries, mostly annealing twins; few low-angle (1º-15º) boundaries
	IPF map / SEM image details	7	• precipitate nucleation and growth, diagnostic for discontinuous precipitation
361 363 365	IPF colour coded maps	8a	• random orientation equiaxed grains containing annealing twins; deformation-induced minor orientation changes within grains and twins
		9a,10a	• deformation-induced local texturing; annealing twins increasingly less visible
		8a,9a,10a	• corrosion-induced cracking ("black" regions) mainly along grain boundaries, but also transcrystalline in figure10a ; intensive intergranular cracking in areas of small recrystallized grains, figures 8a and 9a
	Boundary rotation angle maps	8b,9b,10b	• increasing amounts of low-angle (1º - 15º) boundaries owing to deformation by slip; increasing numbers of deformation twins (narrow, irregular pairs of yellow colour-coded boundaries)

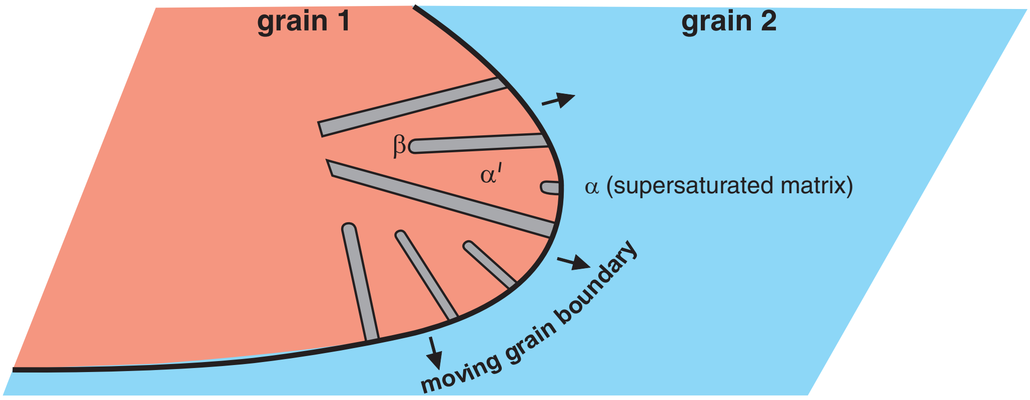


Fig. 1 Schematic of discontinuous precipitation, $\alpha \rightarrow \alpha' + \beta$

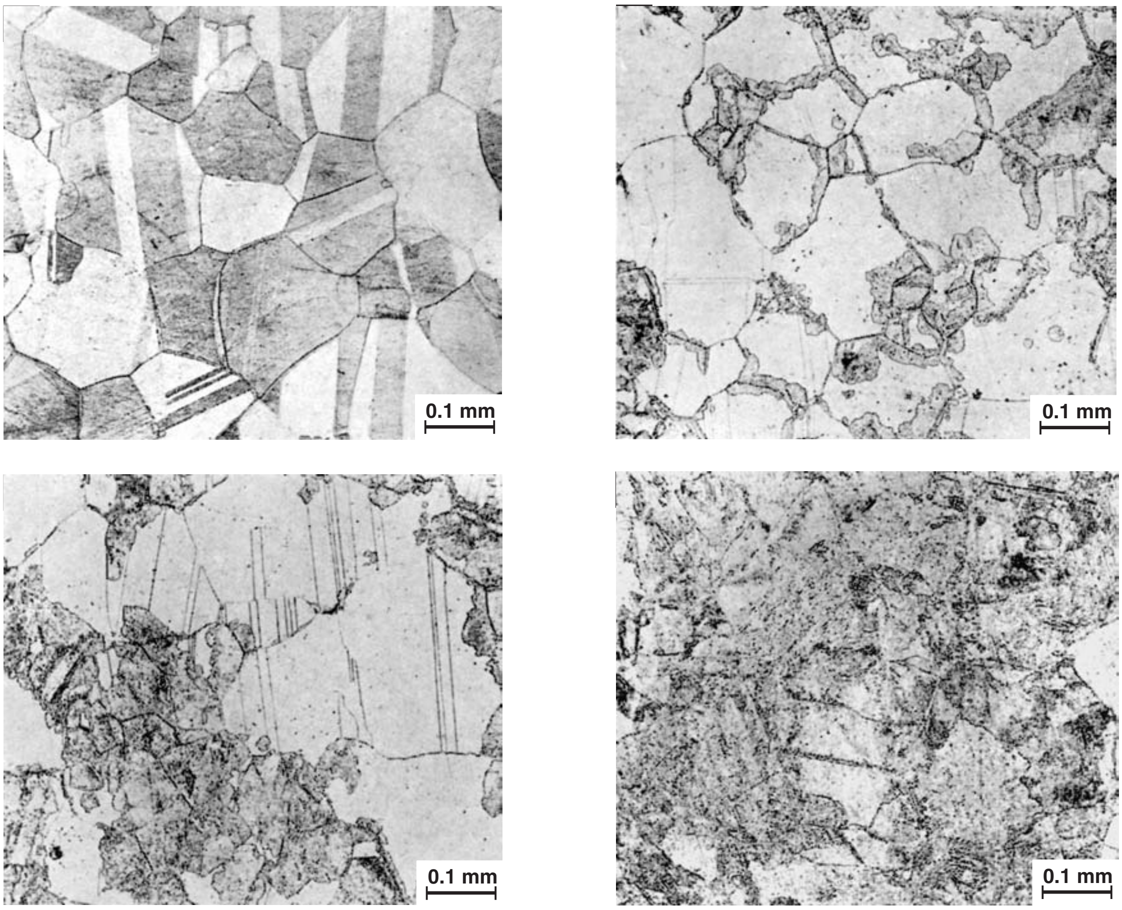


Fig. 2 Discontinuous precipitation of copper at grain boundaries in 800°C solutionised, quenched and 30 minutes aged standard silver, Ag-7.5 wt. % Cu (Norbury 1928):
(a) 250°C aged: precipitation beginning at some grain boundaries
(b) 356°C aged: precipitation further advanced
(c) 440°C aged: precipitation still further advanced
(d) 570°C aged: precipitation practically complete
(photographs reproduced courtesy of the Institute of Materials, London)

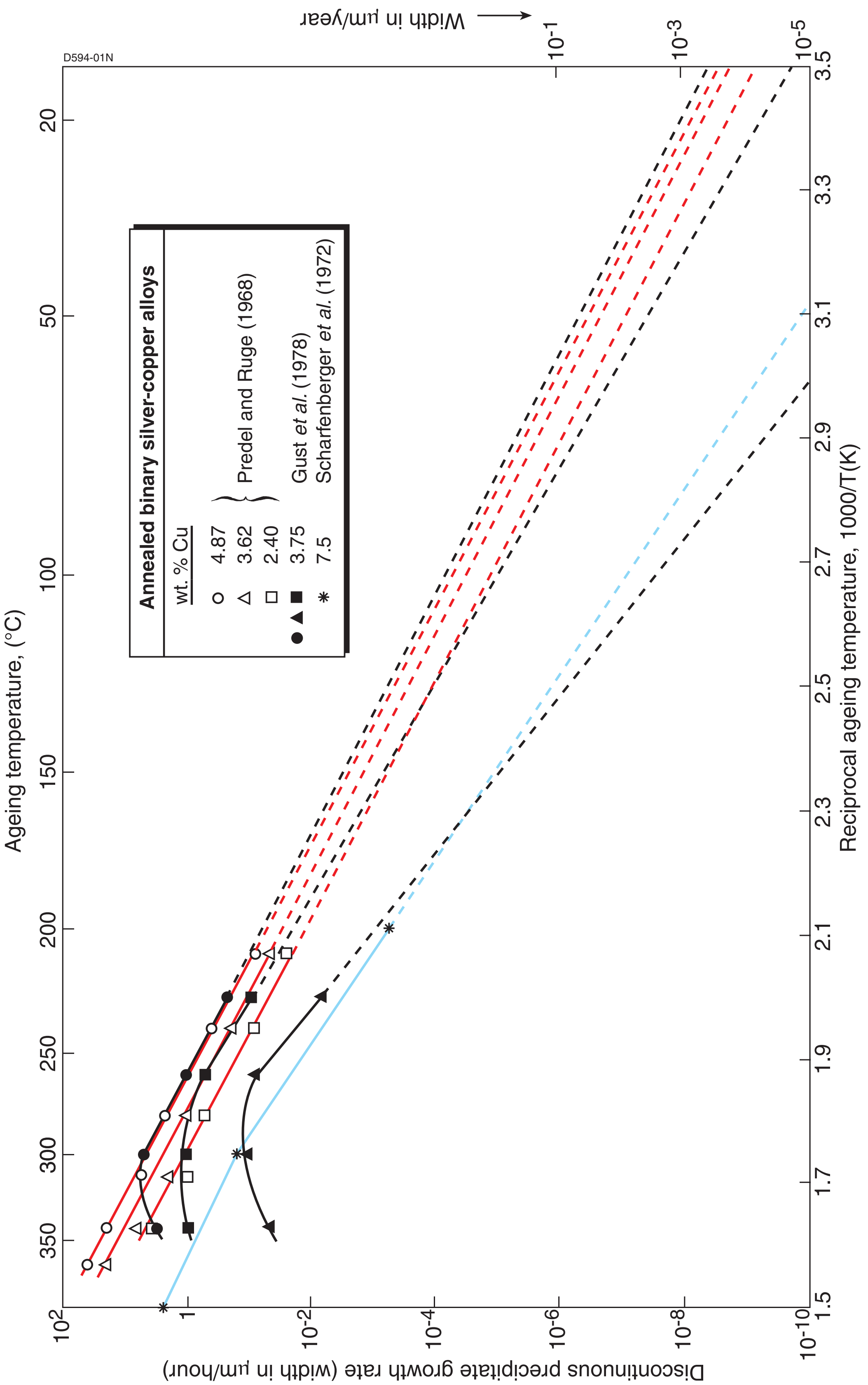


Fig. 3 Temperature dependence of copper discontinuous precipitation growth rates in binary silver-copper alloys: the extrapolations to low and ambient temperatures assume Arrhenius-type reaction kinetics

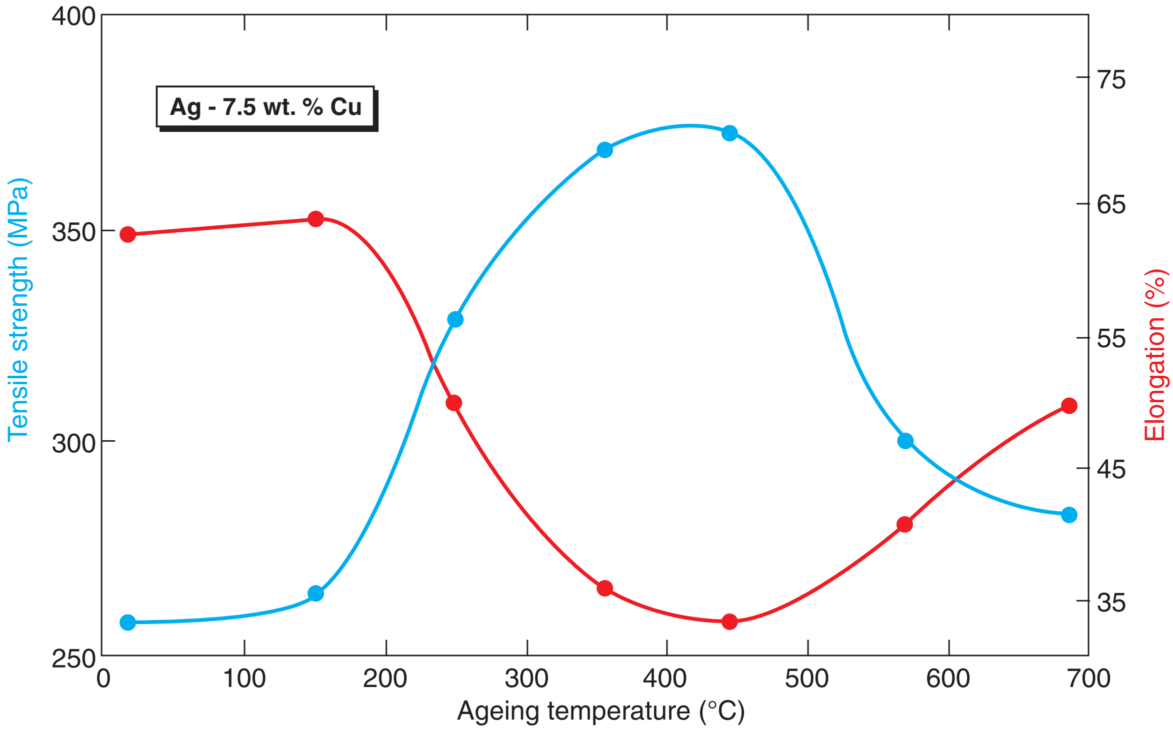
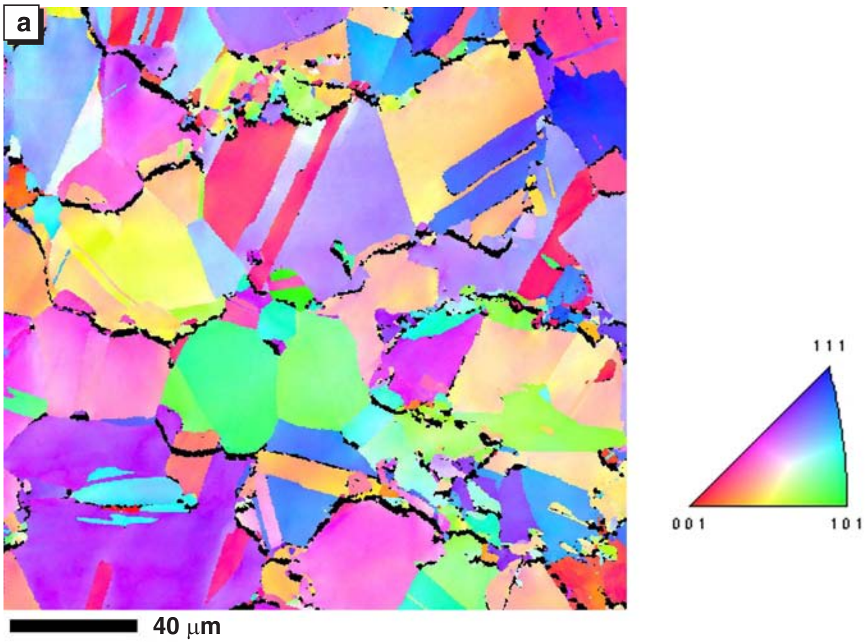
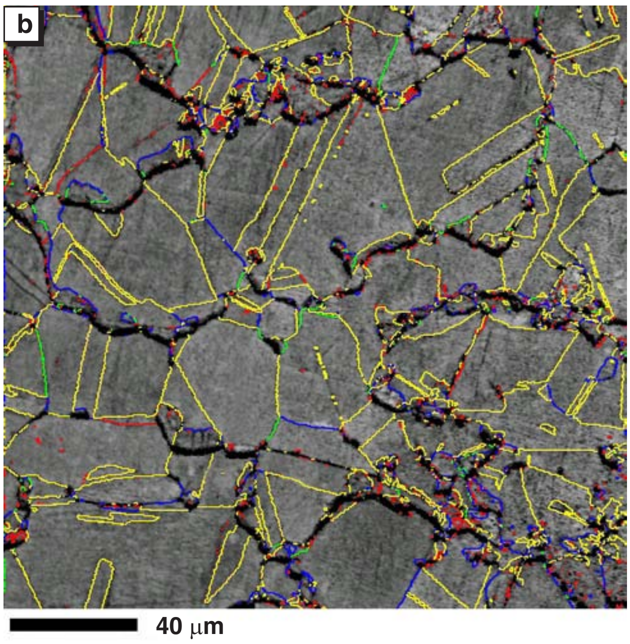


Fig. 4 Effect of 30 minutes ageing on the ambient temperature mechanical properties of 720°C solutionised and quenched standard silver, Ag-7.5 wt. % Cu (Norbury 1928)

Fig. 5 The Gundestrup Cauldron

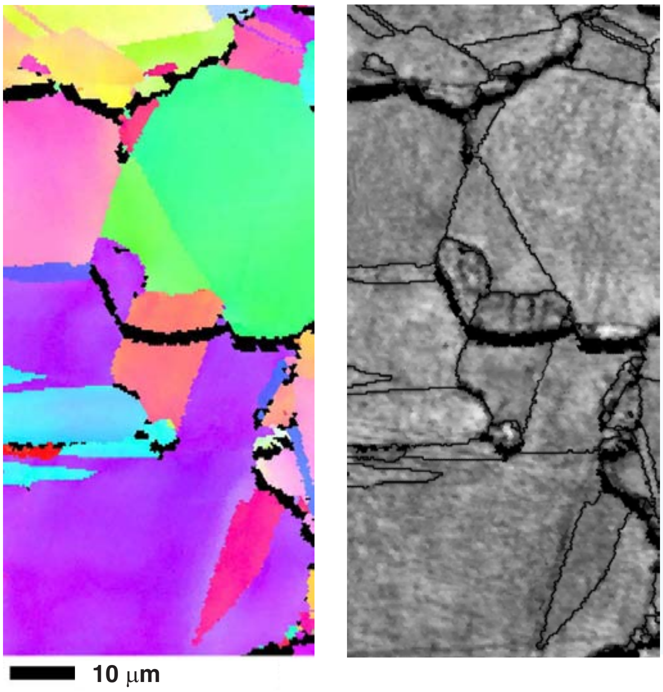




Boundaries: Rotation angle

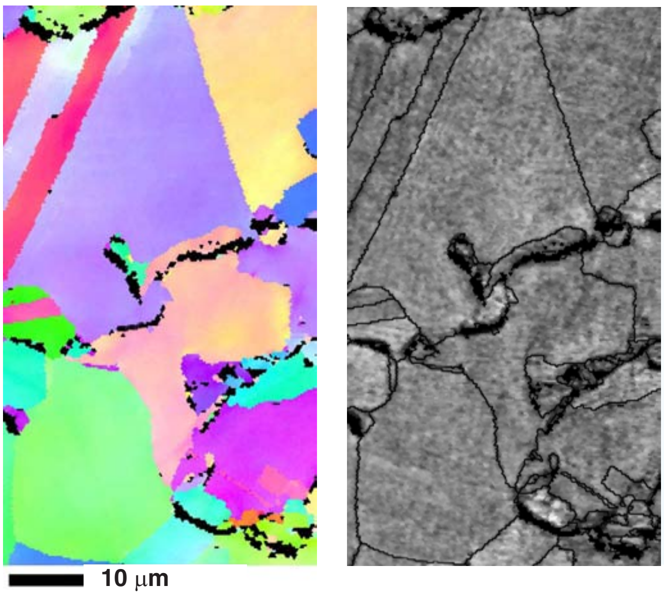
	Min	Max	Fraction
red	1°	15°	0.178
green	15°	30°	0.047
blue	30°	45°	0.158
yellow	45°	60°	0.602
orange	60°	75°	0.015
dark red	75°	90°	0.000
black	90°	180°	0.000

Fig. 6 Orientation and boundary maps for sample 366
a) Inverse pole figure (IPF) [001] colour coded map
b) Image quality (IQ) map with rotation angles



precipitate behaviour

- nucleation at original “green” grain boundary
- growth into “green” grain, changing its lattice orientation to that of the contiguous grain having the “purple” matrix and “brown” annealing twin



precipitate behaviour

- separate nucleations at original grain boundary between “purple” and “pink” grains
- growth in opposing senses: one nucleation into the “pink” grain, changing its lattice orientation to that of the contiguous “purple” grain; one nucleation into the “purple” grain, changing its lattice orientation to that of the contiguous “pink” grain

Fig. 7 Details of precipitate nucleation and growth in sample 366

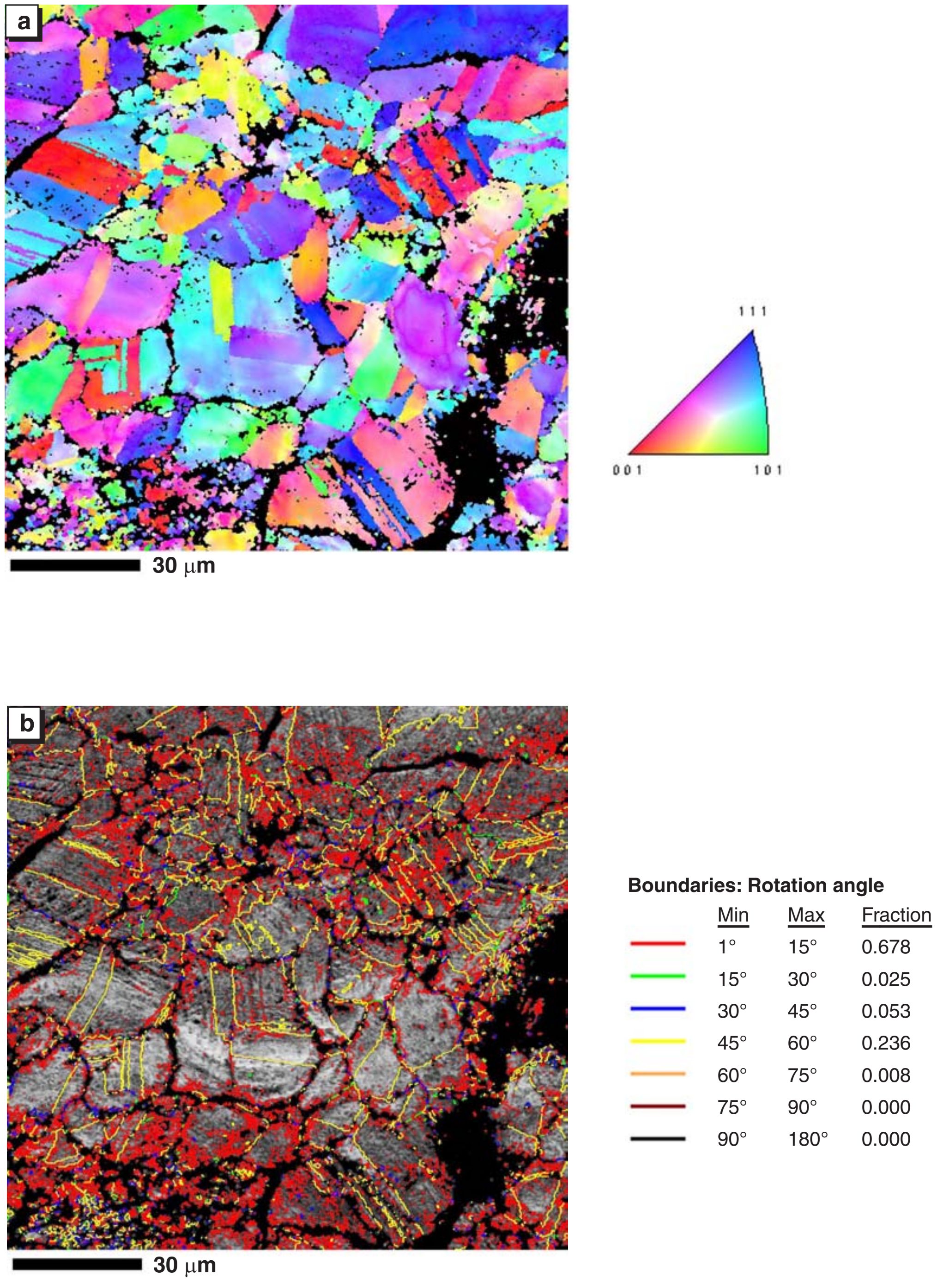


Fig. 8 Orientation and boundary maps for sample 361
a) Inverse pole figure (IPF) [001] colour coded map
b) Image quality (IQ) map with rotation angles

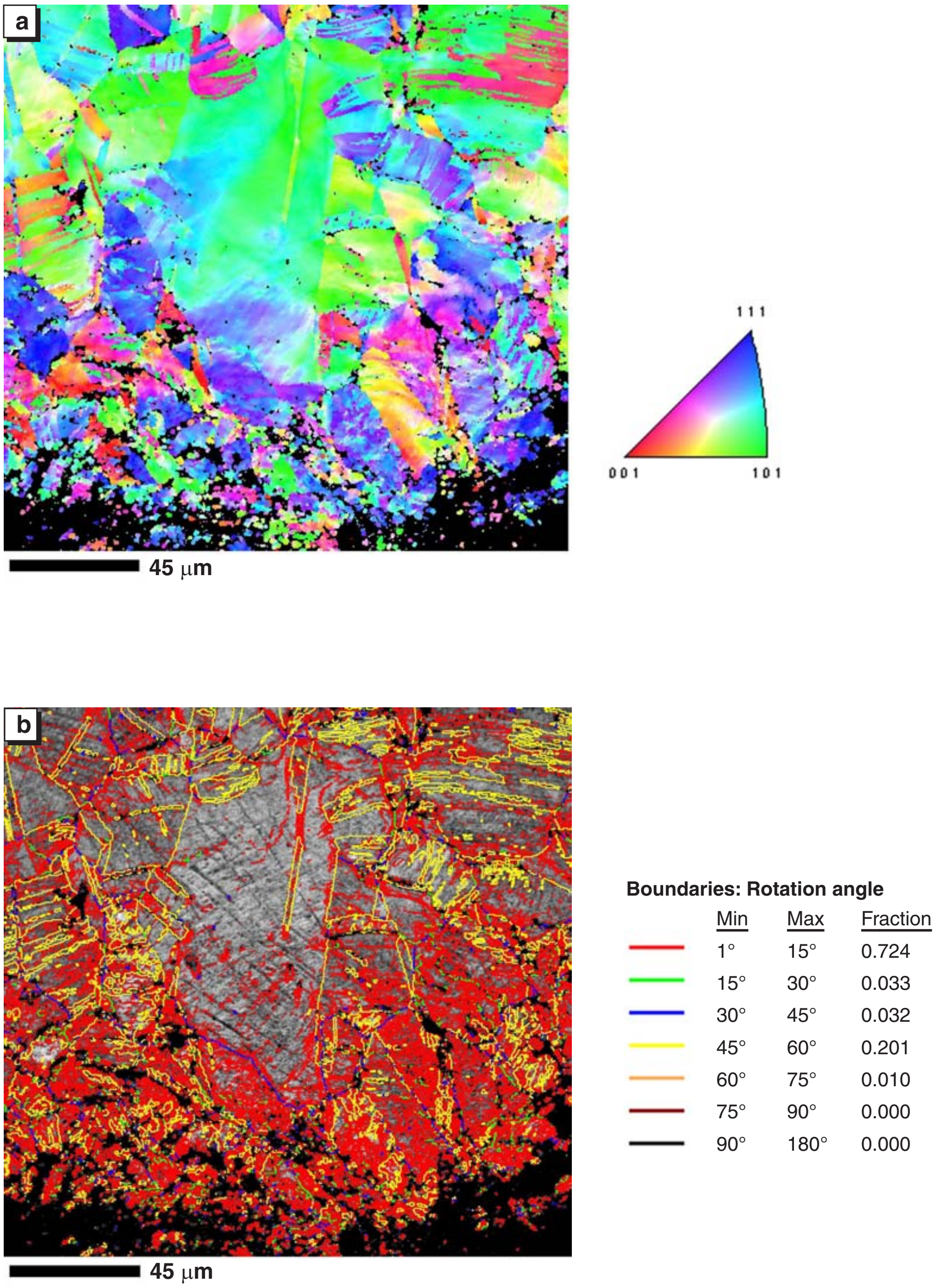
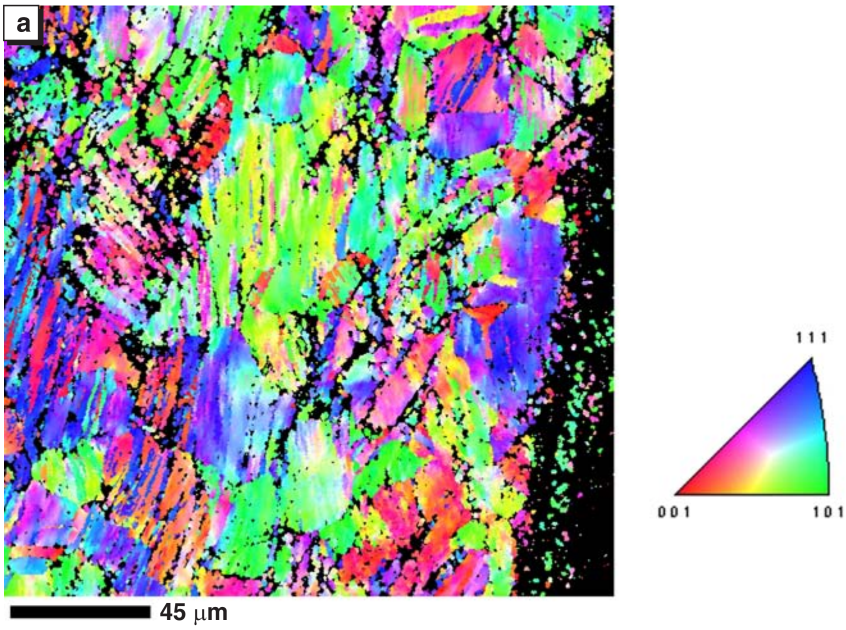


Fig. 9 Orientation and boundary maps for sample 363
a) Inverse pole figure (IPF) [001] colour coded map
b) Image quality (IQ) map with rotation angles



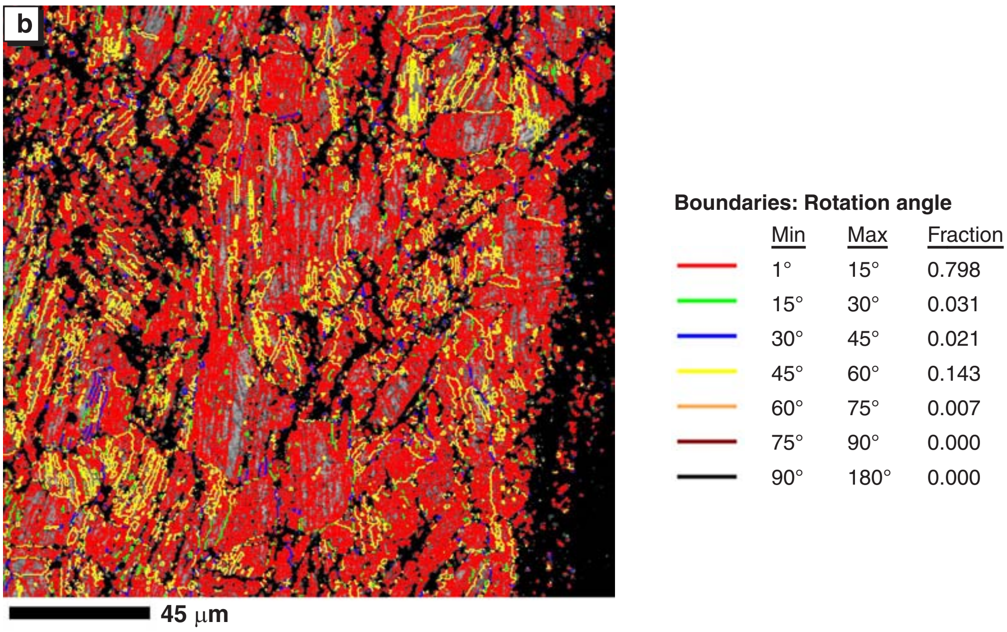


Fig. 10 Orientation and boundary maps for sample 365
a) Inverse pole figure (IPF) [001] colour coded map
b) Image quality (IQ) map with rotation angles

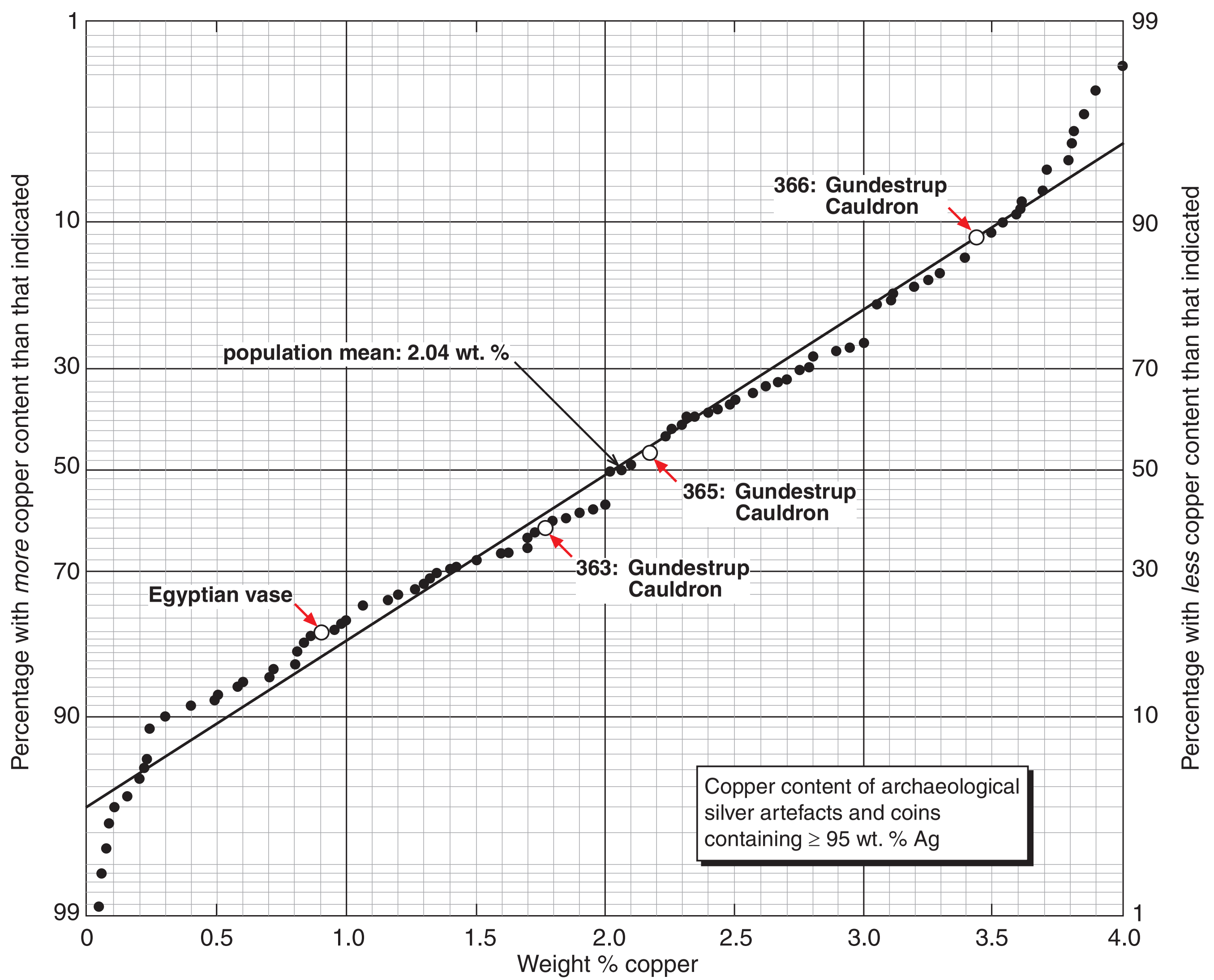


Fig. 11 *Normal probability plot of copper content in ancient silver containing at least 95% silver: data from Lucas (1928), Elam (1931), Caley (1964), Hawkes et al. (1966), Cope (1972), Gordus (1972), MacDowall (1972), McKerrell and Stevenson (1972), Müller and Gentner (1979), Gale and Stos-Gale (1981), Bennett (1994), Perea and Rovira (1995), Wanhill et al. (1998), and this investigation (Gundestrup Cauldron)*