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Applications of Electron Backscatter Diffraction (EBSD) in Archaeology

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<a>ABSTRACT
Electron backscattered diffraction (EBSD) has been used to study samples of archaeological gold, silver, copper and bronze prepared using simple metallographic etches. EBSD maps of orientation and local misorientation revealed the metals' microstructures and deformation substructures, and from this, combined in some cases with information on the crystallographic texture (also determined by EBSD), the methods of manufacture and working of the artefacts were determined.
EBSD was also used to examine discontinuous precipitation at grain boundaries in a silver alloy at a high resolution.

<a>INTRODUCTION
Electron BackScattered Diffraction (EBSD) [(1,2)] is now a very well-established technique in materials science with over 2000 papers published on its use on engineering materials during the last three years but its use in archaeology so far has been very limited [(3,4,5,6)]. This may be due either to archaeological scientists' unfamiliarity with the wide range of different information that can be revealed by EBSD or by the their impression that EBSD involves difficult specimen preparation requiring expensive specialised equipment. This paper presents experimental results from EBSD studies of gold, siver, copper and bronze objects dating from between 13th century BC and the present day which demonstrate that with careful but unsophisticated specimen preparation this technique can give valuable information, unavailable optically, on deformation and ageing which can be used to determine the methods of an object's manufacture and its thermo-mechanical history. It also shows that EBSD can reveal details of the formation of discontinuous precipitation (DP) at grain boundaries which may throw light on DP's role in silver's susceptibility to corrosion and determine if it possible to use the morphology of DP as an unambiguous guide to an object's antiquity.

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<a>EBSD TECHNIQUE

EBSD patterns are formed in a scanning electron microscope (SEM) when an electron beam is scattered by the regular array of atoms in the surface layers of a material and are characteristic of the structure and local crystallographic orientation of the material under the beam. By systematically collecting and analysing these patterns, maps can be built up which reveal the distribution of phases present, show grain sizes and shapes, and give information on the deformation levels in the surface. The orientation measurements taken over an area can also be aggregated to show any crystallographic texture[(7)].

Backscattered electrons have energies only slightly lower than those the incident beam, (much higher than the energies of the secondary electrons that are commonly used for imaging in an SEM), and the backscattered electrons which carry crystallographic contrast have undergone both elastic and inelastic collisions and are diffracted by the regular crystalline array of atoms in the metal grains close to the surface. They can escape from the surface if this happens within a layer that ranges from about 10nm deep for heavy elements like gold to about 100nm for light materials like aluminium. EBSD patterns are usually collected with the specimen tilted to about 70^{o} to increase the proportion of these electrons that escape and so improve the signal-to-noise ratio and such patterns can identify crystallographic orientations to an accuracy of better than 0.5^{o} [(7)].

<b> **EBSD measures of deformation**

The orienations measured at any point on the surface can be compared with either those in its immediate neighbourhood, to give a measure of the local misorientation and so show up sub-grain bounndaries and local strains within individual grains [(8)], or with the orientations of all other points in the same grain to give a measure related to the total plastic strain experienced by that region of the specimen [(9)].

EBSD can measure texture and assist in differentiating between methods of working. Although other effects of deformation can often be observed by optical metallography, in some metals deformation traces may not always be etched successfully and resolution is limited both by the wavelength of light and by the effects of etching. EBSD overcomes these difficulties and also allows us to understand such structures as those where grains are deformed but no internal deformation traces are visible, throwing light on deformation twinning in archaeological alloys.

<b>Surface Preparation

Since EBSD is sensitive to deformation the surface to be examined must be free of any strain induced by mechanical sample preparation and surface relief may distort the patterns so this too needs to be minimised. This can be achieved in various ways depending very much on the material being studied.

In the simplest case a standard metallographic etch can be used to remove the deformed and smeared surface layer left after conventional grinding and diamond polishing. A variation on this is to use colloidal silica (which combines a chemical and a gentle physical attack) as a final polish with or without an etch. A second approach, particularly useful for the softer metals, is to use a chemical or electrolytic polish but the ideal recipes for some archaeological alloy systems, such as As-Cu-Sb,

have yet to be identified. A third method is to use ion milling and cleaning techniques but these require expensive equipment which may not always be readily accessible to archaeologists.

<a>REPRESENTATION OF CRYSTALLOGRAPHIC INFORMATION FOR FACE-CENTRED-CUBIC MATERIALS

Crystallographic planes and directions are conventionally described by Miller indices[7] and represented in space using a stereographic projection[7]. Gold, silver, copper and bronze all have a face-centred cubic structure and due to the very high symmetry of this structure all possible orientations in space can be represented within the fundamental triangle bounded by [001], [101] and [111](Those not familiar with the use of Miller indices to describe crystal planes and directions need only remember that the {111} planes are the close-packed planes , the <110> directions are the close-packed directions and <001>are the x, y and z axes of the cubic structure).Whereas measurements made in the specimen frame of reference (equivalent to the stage position in the microscope) need to be displayed for all possible orientations, any representation in the crystal's frame of reference need only ever consider one 48th of the whole sphere.

<a>METAL-WORKING AND CRYSTALLOGRAPHIC TEXTURE*

Different metal-working processes such as hammering, rolling, or drawing and annealing can lead to alignment of particular crystallographic planes or directions, causing what is known as texture.

Working face-centred-cubic metals usually produces plastic deformation by generating and moving dislocations and this changes the local orientation of the metal crystals. Dislocations generally move more easily on close-packed planes and in close-packed directions and as deformation proceeds grain orientations change so that such favoured planes and directions are closer to the direction of the main applied stresses. In hammering and rolling a metal the constraints on the metal's shape while it is deforming are different so the two processes produce different textures. Drawing a wire produces what is known as a fibre texture.

Table 1 shows which crystallographic planes and directions are preferentially aligned by rolling or drawing a variety of different face-centred cubic alloys.

Table 1 Rolling and fibre textures in fcc metals [10]

Metal	Rolling	Fibre
Cu	(110) [1-12]	[111]
Cu	(123) [1-21]	[100]
Cu -30%Zn	(110) [-112]	
Au	(123) [1-21]	
Au -10 at.%Cu	(110) [-112]	

* Also known as preferred orientation

Ag	(110) [1-12]	

In general <110> tend to align along the direction of compression and <111> tend to align along the tensile direction. Annealing, which recrystallises the structure, does not randomise the metal's texture but leads to complex textures retaining and modifying particular elements of the deformation texture

<a>EXPERIMENTAL

<b>**Samples Examined**

The gold sample, area 2mm x 3mm, was from an Achaemenid period gold bowl taken from close to where it had been soldered to a silver-11% copper alloy sculpture of a winged lion. The gold alloy contained 5.5% copper and 4.5% silver.

Samples from two copper ship's bolts from British warships were examined; one from HMS Pomone, built in 1805 which sank in 1811 and one from HMS Impregnable, built in 1786 which sank in 1799. The sample from HMS Pomone (99%Cu, remainder Ag, As, Bi, Bi, mostly as oxides) was of irregular shape and the sample orientation with respect to the bolt's long axis not obvious from geometry of sample. A section of the bolt from HMS Impregnable had been turned down to make a tensile testing specimen and samples were cut from this so that it was possible to examine both longitudinal and transverse sections

Four copper pennies from the 1797 issue struck at Matthew Boulton's Soho Mint, with a composition similar to that of the copper bolts.

A bronze sickle W. Hungary: BzD-Ha A1 (13th century BC)
Cu - 5.4% Sn, 0.82% As; 0.35% Sb; 0.31% Ni; 0.59% Pb, 0.315 S

Two silver Timurid coins 15th century – Ag, 3.95% Cu, 0.03% Bi, 0.87% Pb, 0.65% Au and one Samanid silver coin 9th-10th C – Ag, 7.7% Cu, 0.85% Bi, 1.01% Pb, 0.04% Au

Modern Ag- 5% Cu, sample homogenised 1hr 800^{o} C then furnace cooled (FC)
Ag- 5% Cu, sample homogenised 20 mins at 700^{o}C then held at 200^{o} C for 72hrs and quenched

<b>EBSD

All EBSD in this study was carried out on a Zeiss Supra 55 Variable Pressure FEG SEM operating at 20kV. The patterns were collected using a Nordlys II Camera with a charge-coupled device area 38mmx28mm and analysed using
Oxford Instruments Channel5 software.

<b>Surface Preparation

All the metals examined were initially polished to a 1μm diamond finish using conventional metallographic techniques and then swab etched. Etching times were generally a few seconds except for the gold which required several minutes. The etches used were as follows:

Gold: *aqua regia*: 30Ml HCl, 20ml HNO_3; the optimum proportions of the two acids varies depending on the silver content of the gold.

Copper: ammoniacal hydrogen peroxide, typically 25ml NH_4OH, 25ml H_2O, 25ml 3% H_2O_2

Bronze: 2g $FeCl_3$, 25ml H_2O, 5ml HCl, 60ml ethanol

Silver: ammoniacal hydrogen peroxide as for copper.
To get good EBSD patterns from the silver coins they then needed a light evaporated C coating (to prevent charging of oxide layer on the surface)

For purposes of comparison one copper bolt was also heavily electropolished using Struers electrolyte D2 at 24V and 17°C

<a>RESULTS AND DISCUSSION

<b>Gold

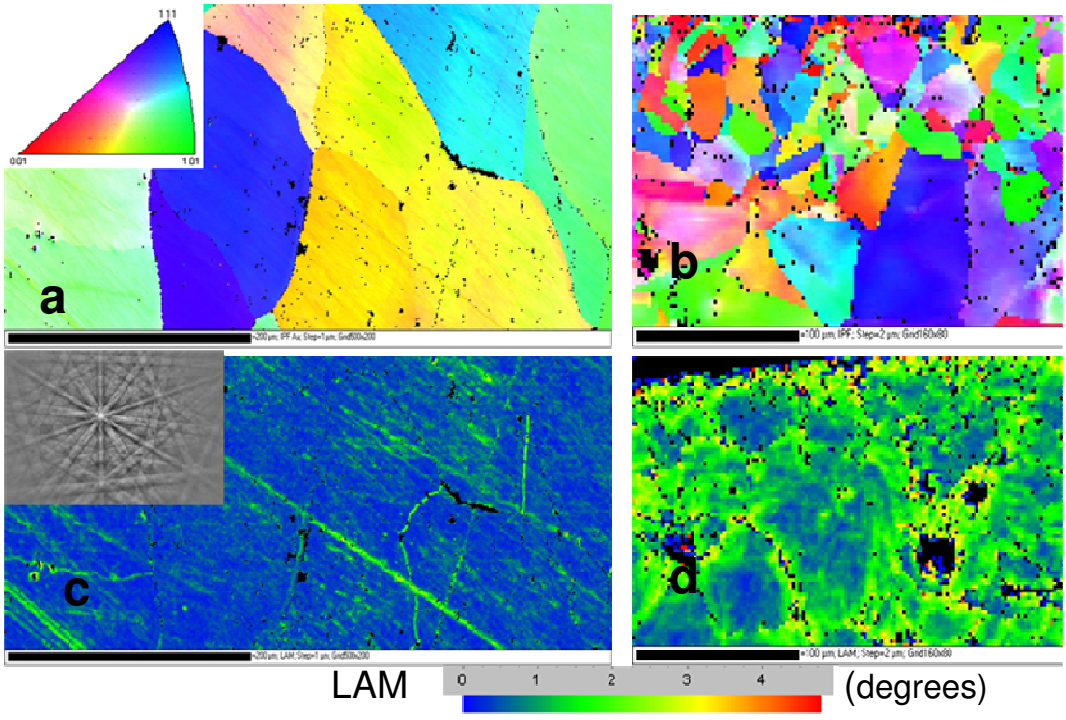

Fig 1 Orientation and local misorientaion maps from Achaemenid gold bowl
a orientation map typical of most of specimen (with inset key to colour coding of surface normal orientations in **a** and **b)**
b orientation map from area near surface of bowl close to soldered joint
c map of local angular misorientation (LAM) of area shown in **a** with inset of typical EBSD pattern from this area
d local angular misorientation map of area shown in **b**

As seen fig.1a over almost all the specimen grains were very large with no twins and little orientation variation within the grains indicating a cast and homogenised structure with no history of cold work. As seen in the inset to fig. 1c, over most of the sample very sharp patterns were obtained which again indicates very low deformation levels and this is confirmed in the local angular misorientation [8](LAM) map which apart from remanent traces of polishing scratches from preparing the very soft metal specimen and occasional low angle boundaries pinned by inclusions shows a LAM (taken over 3µmx3µm grid) of less than 0.5^{o} over the whole specimen. There is no sign of cold work in these homogenised grains within the accuracy of EBSD.

The orientation map and the LAM map in fig.1b and d both show that at one edge of the specimen, corresponding to the outer surface of the bowl close to the soldered joint, there was an area where there was an orientation spread within the grains showing that the surface had been worked and there was a also small area of recrystallised grains. The body of the material may have been homogenised by the heat of the soldering operation to fix the bowl to the winged lion's body. Any heating sufficient to homogenise the grains in the body of the bowl would have been sufficient to cause recrystallisation at any cold worked regions on the surface. The recrystallised grains also show a spread of orientations although when they originally formed they would have been strain free, showing, that the surface had been deformed further after this heating had taken place.

<b>Copper
<b>Ships' bolts
Although the sample of the bolt from HMS Pomone was of irregular shape, the elongation of the stringers of inclusions indicated the projection of the rolling direction on the sample surface and the aspect ratios of the individual deformed particles suggested that the true rolling direction lay within a very few degrees of this plane.

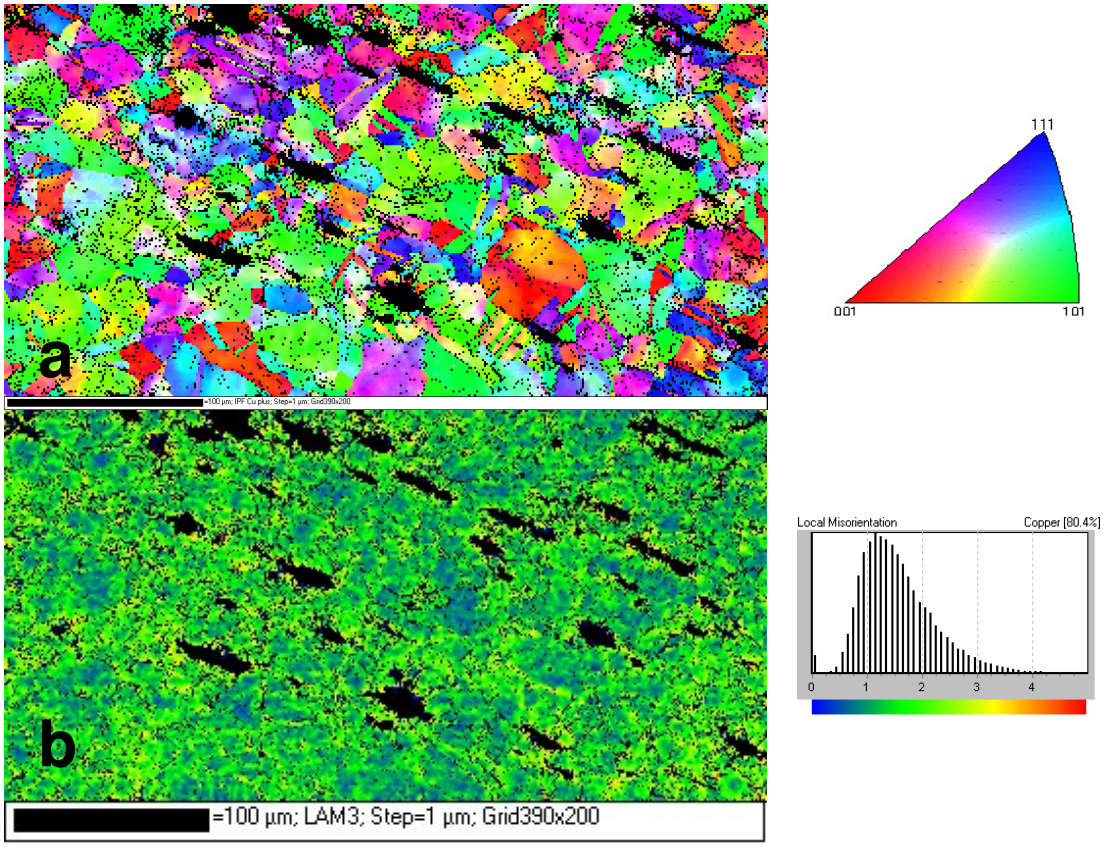

Fig. 2 Copper bolt from HMS Pomone
a Orientation map from close to the rolling plane
b Local angular misorientation map from close to the rolling plane

In fig.2a quite a lot of grains on the orientation map are green suggesting quite a lot of grains with <110> close to the specimen normal, as might be expected for a rolled sample examined normal to the rolling plane. The variation in colour within the grains indicates that there is quite a lot of deformation present. A higher proportion of points were indexed on this bolt if two different copper match units were included with slightly different lattice parameters (although the measured orientations were unchanged). This suggests that there are compositional inhomogeneities in the metal. Fig. 2b shows that over a 3µmx3µm grid the LAM over most of the specimen was between one and two degrees indicating a moderate degree of deformation

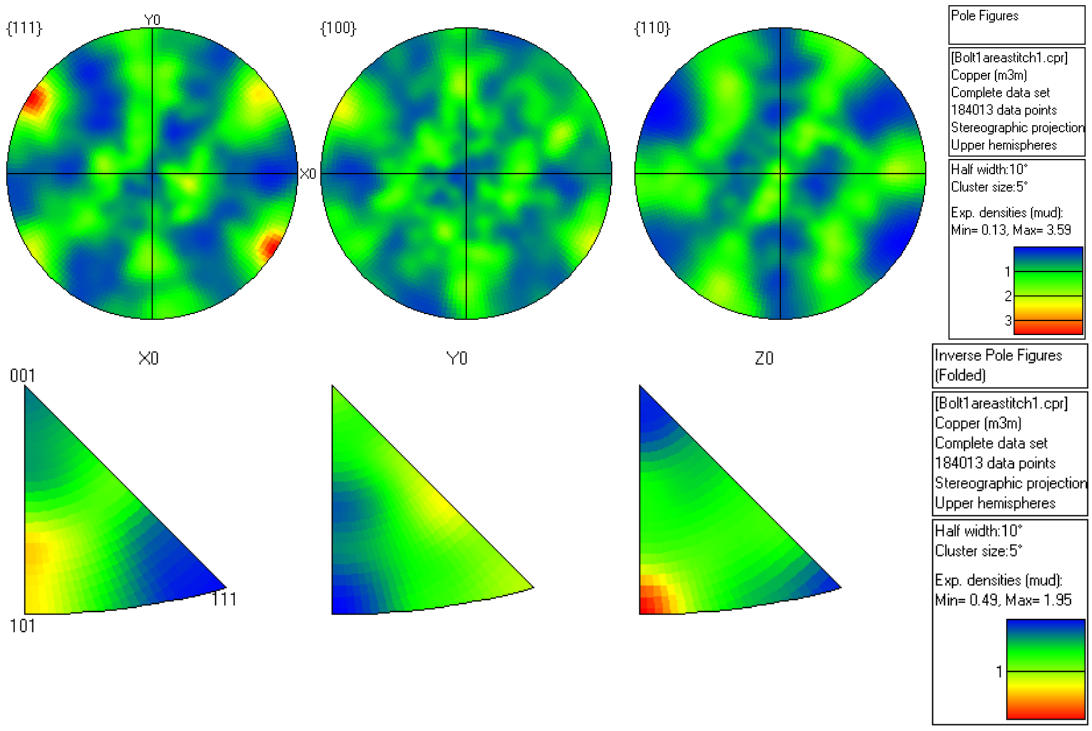

Fig. 3 Results from EBSD texture measurements over approx. 2mm^2 from copper bolt from HMS Pomone

As seen in fig.3 the pole figures (PFs) of the bolt from HMS Pomone show a fibre texture with <111> along the rolling direction which is surprising because <111> directions tend to align along the tensile directions and this is the sort of texture you might find in drawn wire rather than in rolled material and copper ships' bolts of this period were generally rolled.

The inverse pole figure (IPF) shows (as expected from the amount of green in the map of fig.2a) <110> aligned normal to the specimen surface and normal to the rolling direction. This would be the expected texture resulting from compression between two rollers but that this <110> texture is not as strong as the alignment of <111> with the rolling direction .

This bolt's strange combination of a rolled bolt with a clear tensile texture can be explained by the information from Harris [(11)],that 'William Collins of Birmingham took out a patent for ships' bolts on 22 October 1783 claiming to make bolts "which …. will not be subject to the decay that has proved so fatal to those now in use". His process could be used to make either iron or copper bolts. When copper was to be used it was to be as pure as possible. The copper bar was to be gripped between grooved rollers and thereby pulled forcibly through steel drawplates so that small bolts would be drawn out to double their length and large ones to one and a half times.'

This sort of process would produce precisely the sort of texture we see here so we can be confident in saying that the bolt from HMS Pomone was manufactured using William Collins process.

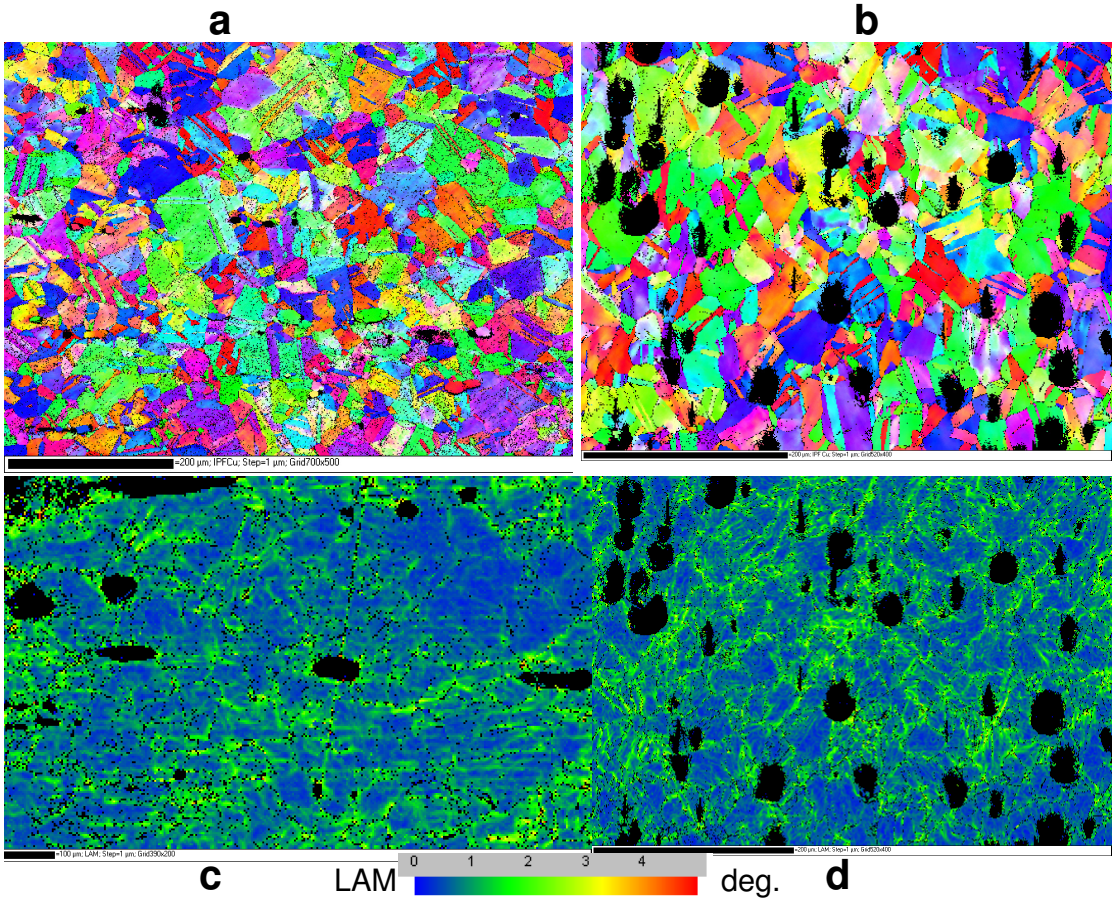

Fig. 4 Copper bolt from HMS Impregnable
a Orientation map of polished and etched cross section (colour key as fig 2a)
b Orientation map of electropolished cross section (colour key as fig 2a)
c LAM map of electropolished longitudinal section
d LAM map electropolished cross section

As seen in fig.4a an orientation map from the bolt from HMS Pomone again showed an orientation variation within grains indicating cold work. In order to be absolutely sure that this cold work couldn't have been introduced during specimen preparation a sample was also prepared by heavy electropolishing and as seen in fig.4b there was exactly the same levels of orientation difference within the grains in both samples. The holes in the electropolished samples are caused by preferential attack of the electropolish at the interface between the copper and the inclusions.

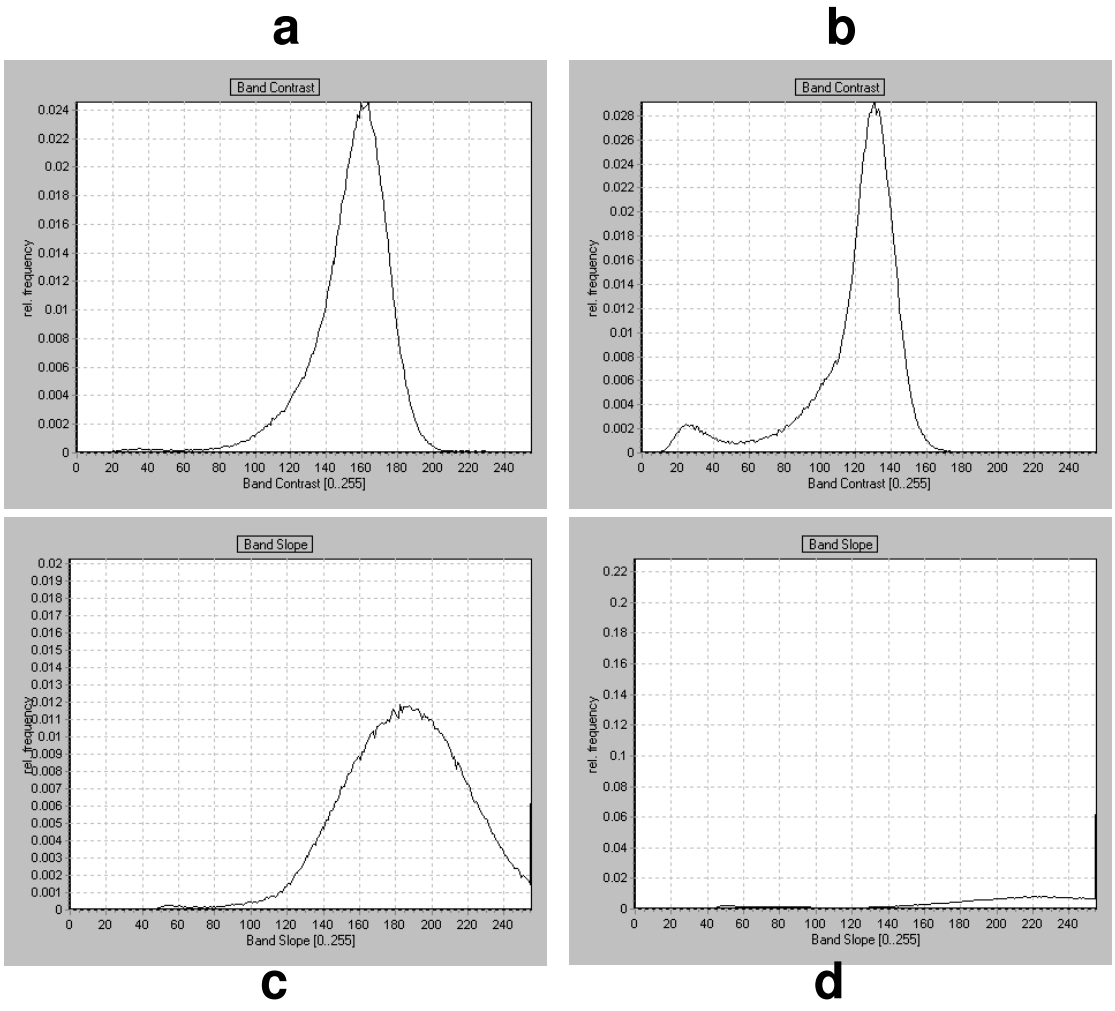

Fig.5 Comparison of EBSD pattern quality from metallographically etched and electropolished samples
a Band contrast histogram from etched specimen
b Band contrast histogram from electropolished specimen
c Band slope histogram from etched specimen
d Band slope histogram from electropolished specimen

Fig.5 shows a comparison of two different measures of the quality of the EBSD patterns obtained with the two different types of specimen preparation. 'Band slope' is a measure of the sharpness of the lines in the pattern with its value increasing with increasing clarity of the line and band contrast. Although the patterns were definitely sharper for the electropolished specimens (band slope peaking at a value of 220 for the electropolished specimen as compared to 180 for the etched specimen), the contrast was actually higher for the etched samples (peaking at value of 160 compared to 130 for the electropolished sample). Since the accuracy of orientation determination from EBSD patterns depends on both their sharpness and their level of contrast this implies that the accuracy of the orientation information from the metallographically prepared samples was comparable to that from the electropolished samples.

The LAM map of Fig4c from the longitudinal section of the bolt from HMS Impregnable shows a lower degree of deformation retained in the grains than in the bolt from HMS Pomone: most of LAM map is blue rather than green in fig.2b Deformation is concentrated in bands parallel to rolling direction.

In fig. 4d the LAM map of the cross section of the bolt from HMS Impregnable also shows much lower general levels of deformation than that from the bolt from HMS Pomone and in the Impregnable bolt the deformation is seen to be localised into a cell structure with pancake shaped sub-grains aligned to the direction of elongation of the inclusions but with no particular other alignment.

The texture of the bolt from HMS Impregnable measured over 9.72 mm^2 of the longitudinal section is shown in fig.6

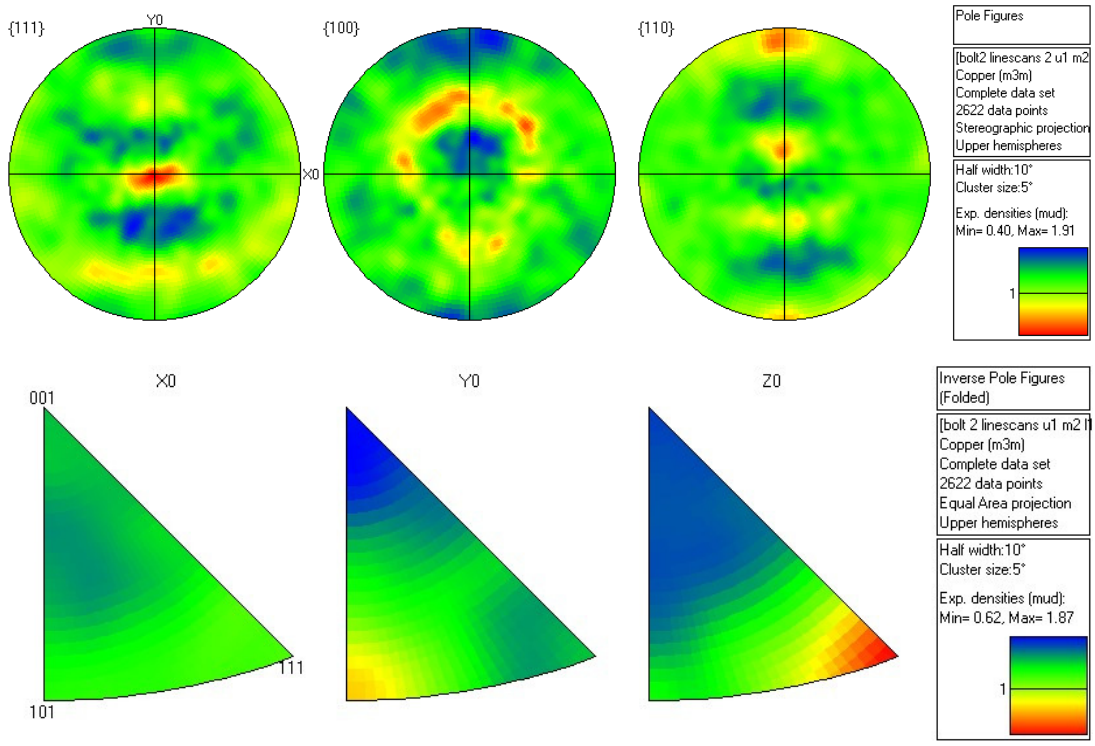

Fig. 6 Results from EBSD texture measurements over approx. 10 mm^2 from copper bolt from HMS Impregnable

It is immediately obvious that the texture of the bolt from HMS Impregnable is very different from that of the one from HMS Pomone. The much more complex texture of the Impregnable bolt suggests that recrystallisation plays a much stronger part than in the first bolt and this is born out by the much lower deformation levels retained in the grains. In the Impregnable's bolt <111> rather than <110> is oriented perpendicular to the rolling direction.

In the late 18th century various different processes were being used to make bolts [(11)] and further work is necessary to determine exactly how HMS Impregnable's bolts

were made but what is very clear is that the two bolts studied were made in different ways

<b> 1797 Boulton pennies

Four of Matthew Boulton's 1797 pennies, which optically and in the secondary electron image of the SEM appeared fully annealed, were examined. Orientation maps from all four showed deformation within the grains resulting from cold striking. For two of the pennies more points were indexed if match units with slightly different lattice parameters for the copper were included although the measured orientations were unchanged: this suggests compositional inhomogeneities in the metal of these two coins.

<b> Bronze

The results from the bronze sickle will be used to illustrate that EBSD can be used to compare quantitatively how much different areas of an object have been worked since its final anneal by comparing the deformation levels at two different places in a tapering sample taken from the sickle's blade as shown in fig. 7.

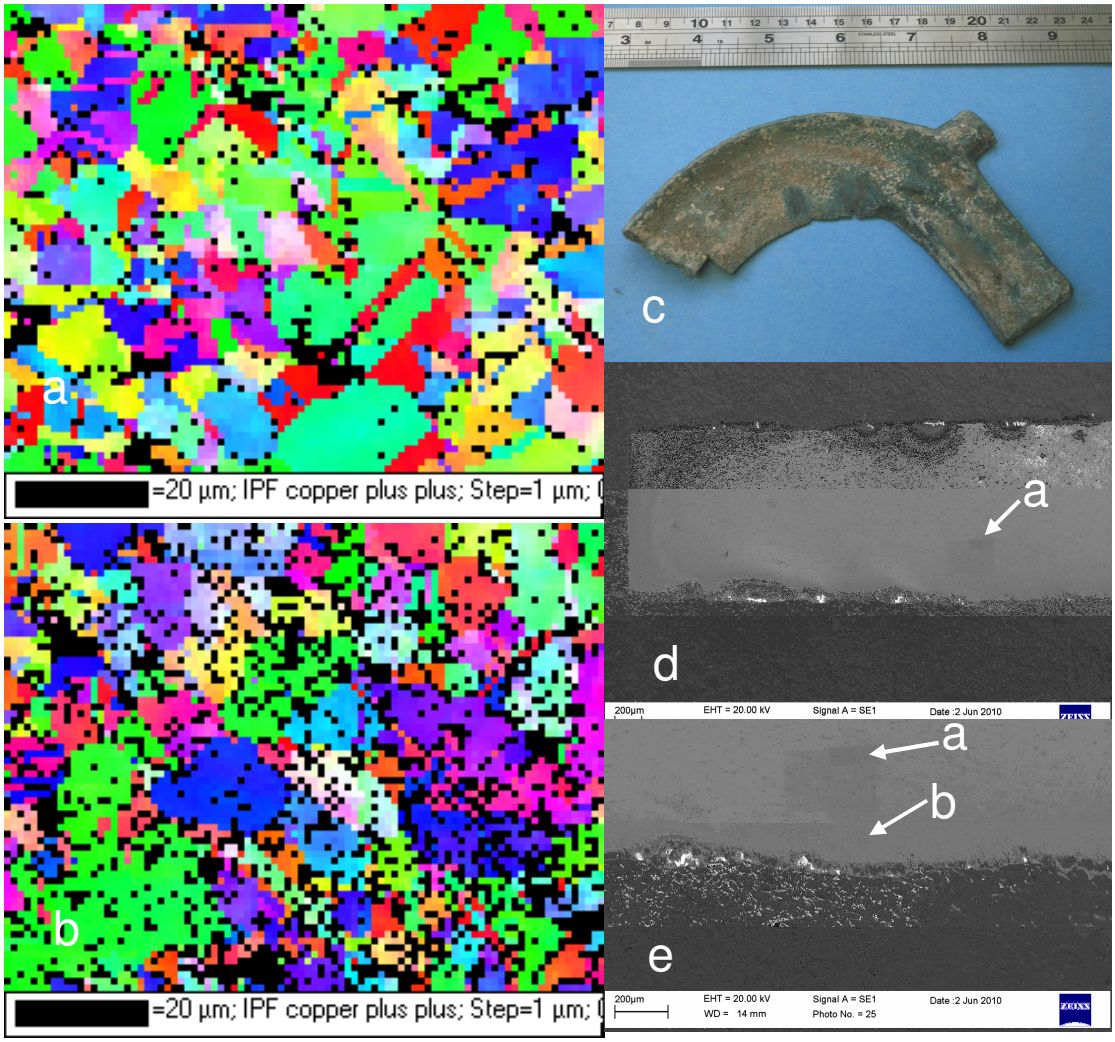

Fig. 7 EBSD maps from near edge of the blade of a bronze sickle
a Orientation map from about 400 µm from edge

b Orientation map from about 100 µm from the edge
c Position from which sample taken from sickle blade
d Position from which map a taken relative to broad end of sample
e Relative positions of a and b

About 400 µm from edge the grain average misorientation [9](GAM) over the area a was 1.4° while GAM measured over area b about 100 µm from the edge was 2.0°. The higher deformation level closer to the blade edge is reflected in the higher proportion of unindexed points and the greater variation in orientation contrast within individual grains. This method could be used to map out quantitatively the amount of working different parts of the object had experienced. About 400 µm from edge GAM was 1.4° while GAM measured over an area about 100 µm from the edge was 2.0°. EBSD measurements of texture over a wider area close to the edge showed no very strong texture but a weak preferred orientation <110> parallel to Y ie normal to the thickness of the thin bit of the blade. This is consistent with hammering.

<B> Silver
Fig. 8 shows orientation maps from the Timurid and Samanid coins

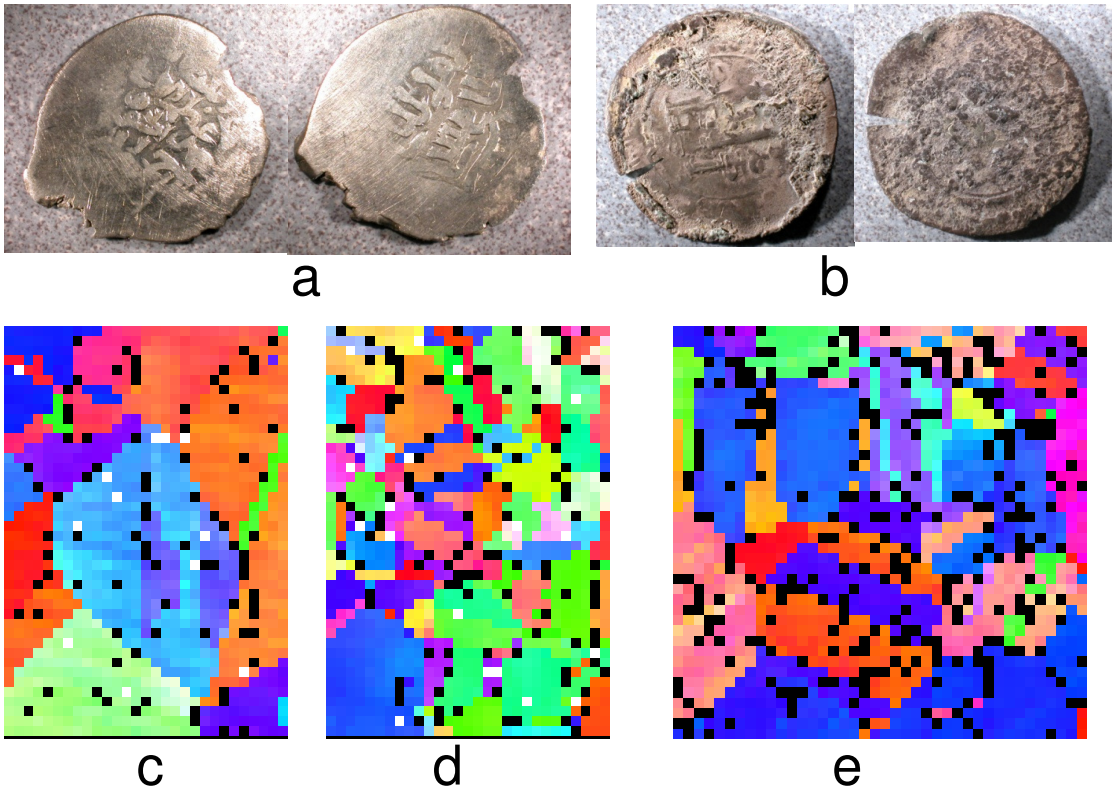

Fig.8 Orientation maps of silver Timurid and Samanid coins
a Timurid coins
b Samanid coin
c Orientation map from a Timurid coin
d Orientation map from the second Timurid coin
e Orientation map from the Samanid coin

As with the Boulton pennies, to optical microscopy the structure looks annealed but EBSD orientation maps show deformation within the grains resulting from cold striking and this can be quantified by measuring the mean local misorientations.

One important question pertaining to silver that EBSD can address is that of discontinuous precipitation and its validity as a marker for antiquity. It has long been recognised that grain boundary changes can occur over archaeological time at ambient temperature, in the form of discontinuous precipitation and diffusion induced grain boundary migration. In the 1970s Pieter Meyers and Francis Schweizer[12] first discussed using discontinuous precipitation of Cu at Ag grain boundaries as an indicator of age but since then there has been very little characterisation of the structures other than by optical microscopy until Wanhill[3] and his co-workers investigated the Gundestrup cauldron using EBSD and concluded that remanent cold deformation rather than discontinuous precipitation was the main cause of corrosion.

In 1998 Dye[13] conducted a series of heat treatments on modern Britannia silver to explore optically the conditions of time and temperature at which different morphologies of grain boundary modifications occur. As determined on an optical scale, she succeeded in reproducing the morphologies of grain boundaries in archaeological silver which shows little stored cold work and her samples provided an excellent model system for characterising these structures more fully. EBSD allows us to investigate the crystallography as well as the morphology and some early results are presented here in fig. 9.

Fig.9a shows a boundary in a sample homogenised and then held at 200^{o}C for 72hrs where several discrete nodules of discontinuous precipitation have formed along the same boundary XY and their growth direction depends on which of the two twin variants of grain A adjoins the boundary. This shows that here the nucleation and growth of the colonies was more influenced by the misorienation across the boundary than by its plane (which simplifies study by EBSD where boundary plane determination requires serial sectioning whereas the grain boundary misorientation is directly available). In both cases the orientation of the colony is the same as that of one of the grains. In one set of colonies the boundary has migrated into grain A and in the other into grain B. (The original position of the boundary is visible in the band contrast image of fig.9b).

The complexity involved in understanding these changes at grain boundaries is well illustrated by the triple junction in an homogenised sample, held 1hr 800^{o}C + FC, shown in fig.9c. In the SE electron image (fig.9d) the structure of the cellular colonies looks very similar to that seen optically but the orientaion map fig 9a shows that in this case two apparently different colonies on each side of the boundary have both formed with the same orientation as grain Q. And there are also small volumes that have grown in the same orientation as grain P. In this case the LAM map (fig.9e)confirms that no low angle b has been left at the original boundary.
EBSD gives us access to the crystallographic information needed to identify the characteristics of grain boundaries at which particular types of changes occur and to help interpret these complex structures. There is still plenty of work to be done.

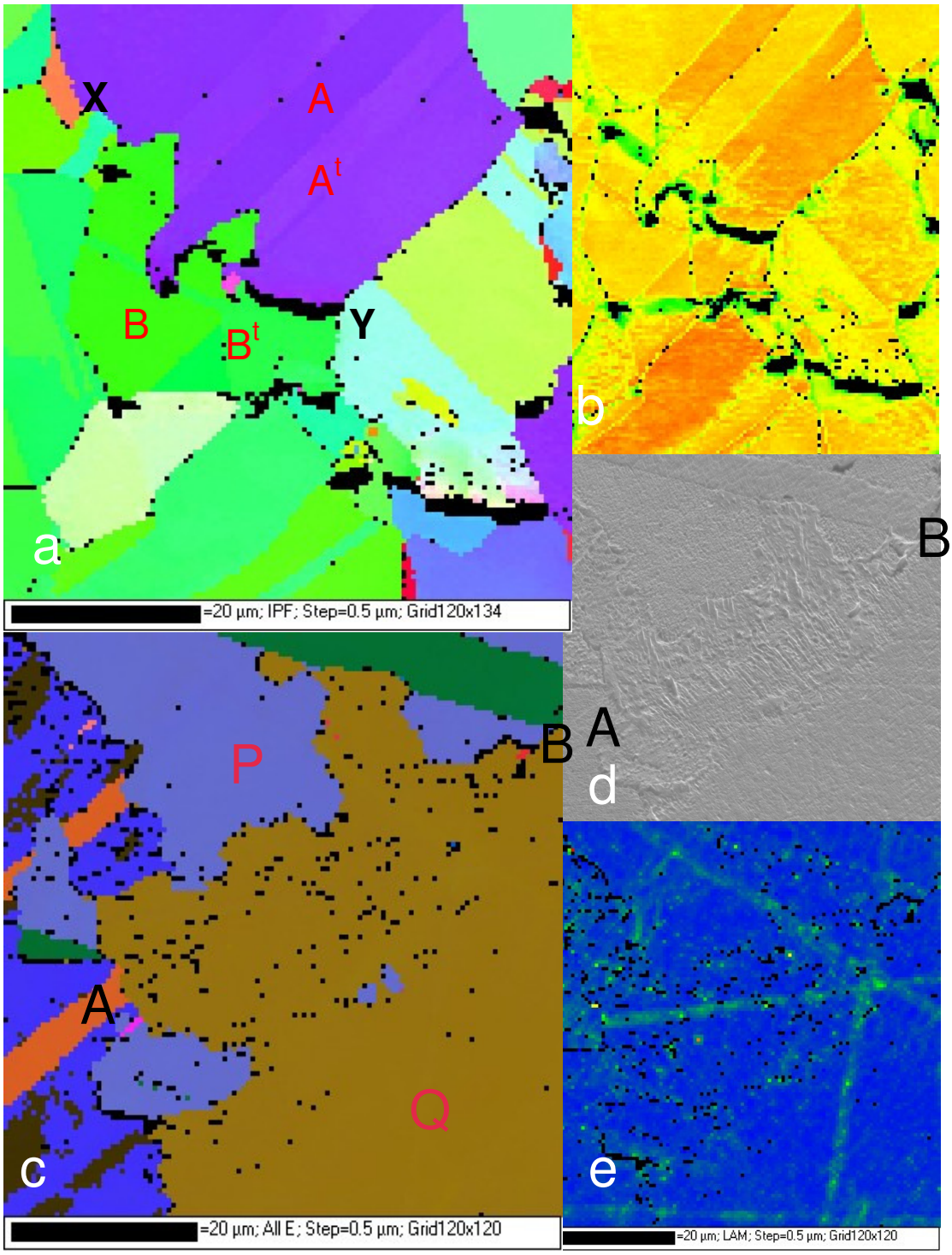

Fig. 9 EBSD maps of modern Britannia silver heat treated to replicate grain boundary morphologies seen in ancient silver

a Orientation map from homogenised sample: held at 200°C for 72hrs

b Band contrast map of area shown in a

c Orientation map around a grain boundary triple point in homogenised sample : held 1hr 800°C + FC

d Secondary electron image of the area in **c**

e Local angular misorientation map of the area in **c**

<A> CONCLUSIONS

EBSD can reveal a metal object's structure, crystallographic texture and distribution of plastic strain and so can be of great use to archaeologists by indicating the methods of manufacture and shaping through their effects on the metal's micro- and macro-textures. EBSD can also be used to investigate grain boundary character and monitor changes at grain boundaries which affect the objects vulnerability to corrosion and so alert conservators to possible problems. Discontinuous precipitation at grain boundaries can be characterised at high resolution with EBSD offering the prospect of determining conclusively what are the implications of discontinuous precipitation in determining an object's age and authenticity. A wide range of metals of archaeological interest can be prepared for EBSD using simple polishing and etching techniques which do not require expensive specialised equipment.

<A> ACKNOWLEDGEMENTS

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List of figures

Fig. 1 Orientation and local misorientaion maps from Achaemenid gold bowl
a orientation map typical of most of specimen (with inset key to colour coding of surface normal orientations in **a** and **b)**
b orientation map from area near surface of bowl close to soldered joint
c map of local angular misorientation (LAM) of area shown in **a** with inset of typical EBSD pattern from this area
d local angular misorientation map of area shown in **b**

Fig. 2 Copper bolt from HMS Pomone
a Orientation map from close to the rolling plane
b Local angular misorientation map from close to the rolling plane

Fig. 3 Results from EBSD texture measurements over approx. $2mm^2$ from copper bolt from HMS Pomone

Fig. 4 Copper bolt from HMS Impregnable
a Orientation map of polished and etched cross section (colour key as fig 2a)
b Orientation map of electropolished cross section (colour key as fig 2a)
c LAM map of electropolished longitudinal section
d LAM map electropolished cross section

Fig. 5 Comparison of EBSD pattern quality from metallographically etched and electropolished samples
a Band contrast histogram from etched specimen
b Band contrast histogram from electropolished specimen

c Band slope histogram from etched specimen
d Band slope histogram from electropolished specimen

Fig. 6 Results from EBSD texture measurements over approx. 10 mm^2
from copper bolt from HMS Impregnable

Fig. 7 EBSD maps from near edge of the blade of a bronze sickle
a Orientation map from about 400 μm from edge
b Orientation map from about 100 μm from the edge
c Position from which sample taken from sickle blade
d Position from which map a taken relative to broad end of sample
e Relative positions of a and b

Fig.8 Orientation maps of silver Timurid and Samanid coins
a Timurid coins
b Samanid coin
c Orientation map from a Timurid coin
d Orientation map from the second Timurid coin
e Orientation map from the Samanid coin

Fig. 9 EBSD maps of modern Britannia silver heat treated to replicate grain boundary morphologies seen in ancient silver
a Orientation map from homogenised sample: held at 200^{o}C for 72hrs
b Band contrast map of area shown in a
c Orientation map around a grain boundary triple point in homogenised sample : held 1hr 800^{o}C + FC
d Secondary electron image of the area in **c**
e Local angular misorientation map of the area in **c**

List of tables

Table 1 Rolling and fibre textures in fcc metals