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Archaeometallurgical residues from Domgay Lane, Four Crosses, Powys

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Abstract

A site at Domgay Lane, Four Crosses, excavated by Cotswold Archaeology in 2005, has produced evidence for copper smelting during the middle Iron Age (4th-2nd centuries BC) from fifteen small cut features, thirteen of which were probably furnaces. The ore from their fills indicates an oxidised zone source, with a mineral assemblage including zincian malachite, azurite, goethite (rich in copper and zinc), quartz, siderite and rosasite. Minor phases include abundant silver minerals, probably mainly acanthite, mimetite and chalcopyrite. Such an assemblage resembles what is known of supergene mineralisation on Llanymynech Hill, 3 km NW.

The small number of copper prills have a variable composition with up to 0.6 wt% zinc and numerous other impurities, but smaller blebs trapped in slag show an even wider range of compositions, with up to 5.7 wt% iron, 2.0% nickel, 1.8% zinc, 5.4% arsenic, 0.8% silver, 0.4% antimony and 14.4% lead. Although the variation shown by individual blebs would be homogenised during the smelting process, there may still have been significant variability in the product, depending on the balance of the ore types in any particular smelt.

Slag was only recovered in minute quantities: a few small prills of flow slag together with fragmented grains of less than 2mm from environmental samples. The flow slag is zinc-rich, but relatively copper-poor, and shows a paragenesis of copper - zincian wustite - various zinc-rich spinels - ferroan willemite - zinc-rich olivine - glass. The fragmented slags include some particles of similar mineralogy to the intact flow slags, but others are dominantly glass with finely dendritic zinc-bearing magnetite, in one example overgrown by delafossite. One fragment was a sinter of ore fragments, quartz-rich sediment and charcoal fragments, bound by a slag rich in zincian wustite.

The furnaces are heavily truncated and their original form uncertain, but they terminated in a basal pit of diameter 0.31 to 0.36m and, in at least one example, were blown through a rectangular block tuyère. It is argued that this was a low-slag crucible-less process. Some of the furnaces had a highly vesicular vitrified clay lining, which may have been crushed at the end of a smelt.

The copper prills have a slightly lower zinc content than other examples of Iron Age high-zinc copper attributed to production in the Llanymynech area. The ores, however, contained a high concentration of zinc and zinc was abundant in the slag. Much of the zinc therefore appears to have been lost to vapour, although significant quantities were captured by the silicate melts of the slag and furnace lining. It is possible that some of the high-zinc bronzes from this region were smelted in a more enclosed structure, or crucible, than the furnaces at Four Crosses. Other impurity elements (iron, arsenic, silver and lead) do correspond to this regional group. In contrast to previous interpretations of the zinc-rich copper from the North Welsh Iron Age, it now appears clear that the ore smelted was not dominantly sulphidic – explaining the lack of large volumes of slag on smelting sites.

Contents

Methods

All materials were examined visually with a low powered binocular microscope as part of the evaluation (Young 2006). All materials were listed on data tables in the evaluation report. The evaluation report identified several distinct groups of archaeometallurgical residue from the site, of which the most significant assemblage comprised materials from copper smelting. These materials derived from a suite of fifteen small cut features and the section of the tables from the evaluation report relating to these features is reproduced here as Table 1. It is the study of material from this assemblage which forms the subject of this report.

From the materials examined for the evaluation reports, a selection of 18 samples (Table 3) was taken forward for detailed analysis. Nine of these (ore, a copper prill and vitrified clay) were from the primary fill of pit 2219 (c2220/2229), six (slag, fine magnetic material and vitrified clay) from the primary fill of pit 2242 (c2243), one (slag) from the primary fill of pit 2034 (c2048), one (copper) from the secondary fill of pit 2210 (c2212) and one (slag) from the primary fill of pit 2373 (c2374).

Electron microscopy was undertaken on the LEO S360 analytical electron microscope in the School of Earth, Ocean and Planetary Sciences, Cardiff University. Microanalysis was undertaken using the system's Oxford Instruments INCA ENERGY energy-dispersive x-ray analysis system (EDX). All petrographic images presented in this report are backscattered electron photomicrographs. The polished blocks for investigation on the SEM were prepared in the Earth Science Department, The Open University. 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 fused beads 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 minor and trace elements was undertaken using samples in solution on the ThermoElemental X-series Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth, Ocean and Planetary Sciences, Cardiff University.

Throughout this report standard mineral terminology is applied to both natural and anthropogenic materials – although artificial phases are no longer strictly considered to be minerals.

The convention adopted in this report is to describe olivine bearing Fe, Mg, Ca and Mn in terms of an olivine on the forsterite-fayalite join (using the notation for instance of Fa95Fo5 for an olivine that is 95% fayalite and 5% forsterite; where Fe/(Fe+Mg) = 0.95) plus figures for the overall percentage replacement by calcium and manganese.

To allow easy comparison between analyses of copper metal, compositions are quotes as wt% element, with the copper and its alloying elements normalised to 100%, excluding oxygen, sulphur, silicon and alumina. Proportions of sulphur are quoted as wt% of the raw analyses.

This project was undertaken for Cotswold Archaeology.

Results

Distribution of the residues

The copper-smelting residues derive from fifteen cut features (Tables 1, 2, 3 and 4). These features occur in three groups, spread out over a NW-SE distance of 130m.

In the NW, features 2034 and 2071 are rather similar. They are sub-circular with diameters of 0.36 and 0.31m respectively. They are both recorded as having a grey fired-clay lining and so are interpretable as furnaces. The geometry of the lining and the shallow depths (0.12m) of the features suggests that they are both highly truncated. Two samples from fill 2039 of furnace 2034 have given calibrated 14C ages of 380BC to 190BC and 370BC to 170BC.

The central cluster includes five features apparently representing similarly-sized furnaces (cuts 2210, 2242, 2272, 2281 and 2313). The circular examples have diameters of 0.33m, 0.31m and, 0.36m while the sub-circular examples have dimensions of 0.28 by 0.33m and 0.28 by 0.34m. These five cuts have depths of 0.09, 0.19, 0.19, 0.15 and 0.12m. Three smaller pits with similar fills are also present in this area (cuts 2252, 2290 and 2297) – they have dimensions of 0.16 by 0.16m, 0.23 by 0.23 and 0.25 by 0.23m. Their depths are 0.12, 0.05 and 0.09m, suggesting that they may be similar, but more heavily truncated.

One pit (2257) is slightly larger at 0.40 by 0.48 and 0.30m deep, but contains a lesser quantity of residues; it is unclear whether this pit is less truncated, or whether it is not a furnace. The latter appears more likely. Two final pits are more elongate: pits c2219 and c2373. Pit (2219) is 0.70 by 0.32m and 0.17m deep, but the residues are concentrated in one, deeper, end of the feature, so the working furnace may have been a similar size to the others in the cluster. Pit (2373) was 0.60 by 0.32m and 0.08m deep. It showed what may have been part of an intact fired-clay lining surrounding a more equant area of the western part of the cut, suggesting a working furnace again of about 0.32m diameter.

Within this cluster, fill 2245 of furnace 2242, gave a calibrated 14C date of 360BC to 270BC or 260BC to 110BC.

The third, SE, cluster, includes a similar furnace (1796), with a diameter of 0.32m and a depth of 0.12m, with a more oxidised appearance than the other examples. Immediately alongside the furnace is a second pit, with similar residues, but without evidence for in-situ burning and with a larger diameter of 0.52m. This pit may perhaps be associated with the copper smelting, but may not actually be a furnace.

Thus the residues occur in fifteen pits in three clusters. Of the fifteen pits, one larger example is possibly not a furnace, and a second slightly larger one may also not be, but the other thirteen are probably the bases of furnaces. Nine of the thirteen have average diameters of 0.31 to 0.36m, three are smaller and shallower, so may be truncated and one may have an approximately 0.32m diameter furnace at one end of a longer cut.

Most of the slag and copper residue recovered from these features comes from contexts rich in charcoal. Some of the vitrified clay may be in-situ, but most appears to be present as debris.

Description of samples

DFC1: The sample comprised two prills of copper 4-5mm in diameter. Prill 1 (Plate 1a) was rather porous, with some marginal alteration and sulphidisation, but with a central region of sound metal (Plate 1c,d). The copper contained abundant inclusions of chalcocite (Plate 1e), giving an overall content of around 3 wt% sulphur, and sparse lead inclusions.

Prill 2 was similar, with sound metal surrounding a central weathered cavity (Plate 1b). As with Prill 1, there was about 3 wt% sulphur as abundant rounded chalcocite inclusions (Plate 1f,g).

Area EDS analyses of the two prills indicate a relatively pure copper (>98.6%) with elevated arsenic (0.7 to 1.1 wt%). One area showed 0.56 wt% zinc and another 0.44 wt% silver. Other potential alloy elements were below detection.

DFC2*:* This was a prill of copper 4mm in diameter (IPlate 2c), with a porous outer zone (Plate 2a,b), but mainly of good metal. The copper showed a high lead content (Plate 2d; 2.2 wt%), with a wide suite of other impurities: 0.4 wt% iron, 0.5 wt% nickel, 1.3 wt% arsenic and 0.4 wt% silver.

DFC3: this sample comprised two copper blebs or prills. Prill 1 (Plate 3a,c-e) is rounded with multiple flow lobes and approximately 5mm wide. It shows well-developed copper dendrites with interstitial Cu2S and lead.

Prill 2 is a hollow structure 6-7mm in diameter (Plate 3b,f). The copper dendrites are well-formed with abundant and varied interstitial lead and lead-bearing phases with chalcocite. The lead–rich phases have not been identified, but include arsenic- and chlorine-bearing species, possibly including lead chlorides and a mimetite-like phase (lead chloro-arsenate).

EDS analyses show prill 1 to have a high iron content (1.3-1.6 wt%), high lead (2.0-2.1 wt%), with moderate nickel (0.4 wt%) and arsenic (0.8wt%) and some silver (0.3 wt%). Prill 2 shows lower iron (0.6 wt%) and nickel (0.3 wt%), but with higher arsenic (1.0 wt% and lead (3.1 wt%). Silver was below detection.

DFC4: this sample (Plate 4) comprises particles with a grain size of 1-2mm magnetically separated from sieved residues. The grains included both angular slag fragments and pieces of ore, many of which showed intense cracking probably from dehydration or decarboxylation reactions.

Several grains were examined in detail.

Ore grains:

Grain 1 (Plate 5e; SOI12): irregular reticulate texture with structureless regions bounded by banded zones. The material, both banded and structureless appears to comprise mainly oxides of iron, but with high levels of zinc (2-4 wt%) and copper (12-13 wt%). One of the structureless regions has a grain approximately 30 µm across of a sulphide grain of uncertain mineralogy, with approximately equal atomic proportions of silver, copper and sulphur, with slightly less of iron.

Grain 2 (Plate 5f; SOI13): this grain has rounded bodies, approximately 100 µm across, possibly originally spherulitic, and often with hollow cores. These may have been carbonates, but now appear to be at least partially oxides, dominated by iron, but with approximately 1 wt% copper and 4 wt% zinc. Towards the outside of these structures they become relatively richer in copper (up to 6 wt%) and flecked with tiny grains of a lead-bearing mineral that was too fine to analyse. The interstices between these rounded bodies are infilled with a second generation of oxides after a sparry carbonate mineral, again dominantly of iron oxides with 3 wt% copper and 5 wt% zinc. All the zones show some silicon (up to 4 wt%) and calcium (up to 2 wt%).

Grain 3 (Plate 5g; SOI14): this is an intensely cracked grain with a reticulated texture. The core region of the structureless zones is dominantly iron oxide, with moderate silicon (5 wt%) and approximately 3 wt% of both copper and zinc. These zones pass outwards into banded zones in which the copper content rises to about 15 wt%. The structureless zones shows radial cracking, presumably from dehydration, with the widest cracks close to the core of the zones. The oxides show trace levels of lead (<1 wt%).

Slag grains:

Grain 4 (Plate 5a,b; SOI1, SOI2): slag fragment with localised secondary botryoidal coating. Grades from a glass with relict sediment grains through a zone about 800µm thick of a glass-rich slag with coarse, and possibly partially resorbed, primary spinel (up to 60 µm across, approximately magnetite with 24-35% gahnite) and an elongate zinc-bearing olivine (up to 1mm in length and 150 µm in width, with a composition equivalent to Fa87Fo13 substituted with 15% of Zn_2SiO4), into a zone about 1mm thick in which the texture becomes finer grained (<50 µm) and more granular spinel with a fine-grained groundmass. The outer part of the glassy zone in particular bears abundant spherical blebs of copper. The copper compositions of ten analysed blebs showed high levels of iron (0.7 to 4.7 wt%, an average of 2.94 wt%) and zinc (0.4 to 1.1 wt%, with an average of 0.87 wt%). Only one bleb had detectable nickel (0.35 wt%), one had detectable arsenic (0.53 wt%) and two had detectable silver (0.38 and 0.41 wt%). No blebs had detectable lead.

Grain 5 (Plate 5c,d; SOI3, SOI4): slag fragment with rounded and possibly resorbed zinc-substituted magnetite associated with irregular blebs of copper. Six analysed copper blebs showed a high iron content (range 2.2 to 4.2 wt%, average 2.9 wt%). Two blebs showed detectable arsenic (0.9 and 1.1 wt%), but no blebs showed detectable nickel, zinc, silver or lead. These phases were set in a poorly-preserved silicic glass with 9-11 wt% iron, 11 wt% calcium and 18-20 wt% zinc and 3 wt% barium.

Grain 6 (Plate 5h, Plate 6a-b; SOI15, SOI16, SOI17): This slag grain shows two marked layers. The first has a glassy matrix which bears elongate magnetite dendrites up to 500 µm in length, with the magnetite having substantial aluminium, magnesium and copper substitution. This zone has an overall composition with around 4 wt% copper. In the second zone the copper content exceeds 20 wt% and the magnetite has reacted to form an iron-copper oxide, probably delafossite ($CuFeO_2$; this case not quite stoichiometric, having a small amount of substituted aluminium). The delafossite extends into the glassy matrix in a tabular habit.

Grain 7 (Plate 6c,d; SOI18, SOI9): This slag fragment is dominantly glass (silicic, with 4 wt% calcium, 3 wt% potassium, 7 wt% iron and 6 wt% of copper and zinc). The glass bears delicate dendrites of magnetite (with aluminium, magnesium and major zinc substitution (approximately 43% franklinite). The glass bears abundant spherical blebs (5-10 µm in diameter) if copper. The copper has a high iron content (range 2.5 to 3.7 wt%, average 3.0 wt%), but no other alloy elements at detectable levels.

Grain 8 (Plate 6f,g; SOI21, SOI22): This slag grain shows a fresh, coarse, void rich magnetite phase (with low levels of magnesium, aluminium, copper and zinc substitution) in glass. The glass is moderately silicic, with a high calcium content (15 wt%) but low potassium (3 wt%), moderate iron (7 wt%), moderate copper (7 wt%), moderate zinc (4 wt%) and traces of arsenic and lead (both <1 wt%). The slag bears blebs of copper with high iron (3.0-3.9 wt%, average 3.4 wt%), but no other detectable impurities.

DFC5: a small piece of dense flow slag with a cross section of 10mm by 13 mm. One piece of the flow was mounted for examination on the SEM, another was crushed for chemical analysis.

The section shows multiple lobes to the flow (Plate 7c), with slight compositional variation. The primary copper droplets were compositionally rather variable. The majority of analysed blebs had a high iron content (4.2 to 5.7 wt%, average 4.85 wt%). Only one of these high iron blebs had other detectable impurities, with 1.83 wt% of zinc and 1.4 wt% of arsenic. One bleb had a low iron content (1.3 wt%) and a variety of other elements: 0.6 wt% of zinc, 0.4 wt% of nickel, 0.4 wt% of arsenic and 1.9 wt% of lead.
The high iron content of the copper means that the sulphide overgrowths present on many blebs are of mixed phases, with the EDS analyses suggesting a mixture of FeS and Cu_2S (Plate 7d,g,h, Plate 8b,c).

The next phase appears to be zincian wustite with 5.2-8.6 molar% ZnO. This phase forms dendrites of conventional wustite-like form (Plate 7a,d), as well as being found in less regular form in the carious centres of large euhedral zinc-rich zoned spinel crystals (Plate 8d). In the core of the prill there are even, non-carious, spinels with a composition of approximately 60% magnetite, 20% gahnite, 17% spinel *ss* and 2% hercynite, which overgrow the zincian wustite (Plate 7d, Plate 8a). The carious spinels are found mainly in the outer parts of the prill (Plate 8d and seem to show complex variation between a similar composition and composition close to 28% magnetite, 56% gahnite, 6% hercynite and 10% spinel *ss* as an outer zone on more iron- rich cores. The most iron-rich analyses of zinc - bearing spinels approximate to 55% magnetite and 45% franklinite.

In the outer parts of the prill the spinels may be reduced to small (approximately 5 µm) grains, possibly indicating resorption (Plate 8c).

The spinels are followed by laths of zinc-rich olivine (Plate 7e, Plate 8d), which forms the bulk of the slag. Lath size varies, but they are locally up to 200 µm in length. The composition of the olivine can be described as 65% kirschsteinite, with about 35% monticellite (i.e. a magnesio-kirschsteinite), onto which is superimposed approximately 9% substitution by zinc.

DFC6: this sample is a flow slag with a cross section of 10mm by 6mm. One piece of the flow was mounted for examination on the SEM, another was crushed for chemical analysis.

The slag is relatively coarse-grained, with coarse phenocrysts and metal droplets in a glassy matrix (Plate 9).

The slag is rich in droplets of metal, some partially sulphidised and some oxidised. Some of the smaller blebs show voids suggestive of the former location of lead, but for the central regions of larger droplets the lead is still in place (Plate 9d,f). Bulk analyses of these larger droplets give 12 to 14 wt% lead, 3.1-4.3 wt% arsenic, 1.1 wt% nickel and up to 0.5 wt% iron. Zinc was below detection, but was found in some spot analyses of the copper phase, so may present at levels of up to 1.2%. Antimony was detected in one area of the copper phase at 0.4 wt% (at which level it would be close to, or below the detection limit in the bulk analysis).

The areas of oxidised metal are marked by patches of blebs of zincian-wustite (Plate 9e-g). Zinc-bearing spinel group minerals occur widely in the sample, mainly with a grain size of less than 20 µm (Plate 9a). They are typically of a composition equivalent to 70% magnetite, 20% gahnite and 10% franklinite. These spinels are commonly enclosed by both olivine and willemite. In one instance euhedral spinel group minerals occurred within the glass; these were more

aluminous with a composition equivalent to 22% magnetite, 62% gahnite and 16% hercynite.
Much of the texture is formed by two silicate minerals with rather similar size and morphology, forming large quench-textured laths and more equant grains up to 600 µm across (Plate 9a-c). The earlier of the two phases is a magnesium-iron-zinc silicate, probably interpretable as a willemite with an unusually high iron substitution, apparently ranging from 26 to 45%. Magnesium substitution ranges from 4 to 7%.

The second of the two is an olivine of approximately Fa95Fo5 with about 4-5% substitution by calcium and 6% by zinc.

The sample shows a high degree of fracturing, with the cracks commonly filled by secondary lead-rich phases (e.g. Plate 6a).

DFC7, DFC8 and DFC9: sample DFC7 was a polished block for SEM examination, showing a section through a typical piece of vitrified clay. DFC8 was a sample for bulk chemical analysis of the less vitrified part of this material and DFC9 was the highly vitrified surface layer. Unfortunately, problems with the surface of DFC7 prevented its examination on the SEM.

DFC10 and DFC11: DFC10 was a sample for bulk chemical analysis of the less vitrified part of this material and DFC11 was the highly vitrified and reddened surface layer.

DFC12: this sample was a section through a vitrified clay block, similar to the material sampled for DFC10 and DFC 11.

The section (Plate 10a) shows the development of vesicles with the size of vesicle increasing progressively from the inner face of the vitrification, where the vesicles first appear, through to about 1mm below the surface, where the vesicles attain sizes of up to 3mm across. The vesicles are somewhat tabular, aligned with the surface. Many vesicles show convex inwards faces, suggesting deflation of the vesicle as adjacent ones expanded.

The density of quartz grains decreases outwards through the vitrified layer, with the surface containing very few, and very small, relict grains. The glass contained a significant quantity of small grains of titanium-bearing minerals and in the innermost areas there are relicts of larger grains (e.g. Plate 10f).

Only the outermost 2mm of the section bears copper droplets (i.e. to a depth just between the outermost large vesicles), within a glass that is slightly enriched in zinc and lead (Plate 11a-d). The larger droplets examined all proved to have entirely oxidised to cuprite, but some of the very small droplets were copper metal. The impurities in the fresh droplets were limited to iron at about 2 wt%. A bleb formed largely of cuprite showed silver-rich inclusions (Plate 11b), the mineralogy of which is uncertain, although one was possibly of metallic silver.

DFC13: this sample was a section through a vitrified clay block, similar to the material sampled for DFC10 and DFC 11.

The mounted specimen was largely equivalent to material in the outermost layer of the vitrified material in DFC12.

As with DFC12, many of the blebs of copper in this specimen were oxidised (Plate 12d). One with a reasonably intact metal core gave analyses indicative of copper with 0.6 to 0.7wt% arsenic (Plate 12b). One sample showed 0.3% of nickel – very close to the detection limit.

DFC14: this sample was a small fragment of residue of rusty appearance. In section it proved to be a mixture of particles interpreted as part-reacted ore fragments (Plate 13a), quartz-rich sediment (Plate 13d) and mineral-impregnated charcoal fragments (Plate 13c), bound together by a slag phase rich in what are probably hydrated oxides of both iron and copper (Plate 13b). It is probably representative of other material described in the evaluation as ferruginous furnace floor sinter.

The material appears to be highly altered, with hydrous oxides apparently replacing the original anhydrous phases. Much of the material shows a network of iron oxide blebs, probably originally wustite, partially set in a matrix rich in copper oxides, but the original mineralogy of this texture is uncertain.

DFC15/16: this sample comprised a collection of particles isolated from sample 126, hand-picked as appearing visually to be fragments of copper ore. All showed a green colour. The particles were divided to provide material for a bulk analysis (DFC15; ICP-MS only), with two pieces mounted as a polished block for SEM examination (DFC16).

Particle1: the grain is up to 12mm across and at low magnification appears to be an amalgamation of small green bodies. In section, the central part of this piece shows a texture of relict grains pseudomorphed by copper-zinc carbonate, probably mainly zincian malachite, as radiating sheaves of elongate crystals.

In the interstitial areas between the pseudomorphed grains the malachite encloses numerous quartz grains, often subhedral and typically of less than 50 µm (Plate 14c). Similar quartz-rich material forms a matrix around the exterior of the particle and the malachite crystals can be seen form coarse radiating sheaves at the margins which are invasive to this matrix (Plate 14f).

Some of the pseudomorphed grains are picked out (e.g. SOI9, Plate 14e) by tiny (~1 µm) blebs of an unidentified phase containing oxygen, sulphur and silver (up to 43, 14 and 38 atom% respectively).

A lead sulphate, probably anglesite, occurs in a form suggesting it may be partially pseudomorphing galena, in grains up to about 700 µm across (e.g. Plate 14a, d).

The grain also shows probable pseudomorphs after siderite (e.g. Plate 14b), but these were not analysed (similar grains were seen, and analysed, in DFC18 particles 1 and 3, see below).

Particle 2: this particle has a very irregular shape (Plate 15a), approximately 10mm by 5mm in cross section. The surface appeared mainly green, suggesting the grain was formed of copper minerals, but on sectioning the interior was found to be brown iron oxides and the copper minerals merely a superficial coating.

Analysis showed that the interior of the grain was formed by relict grains within a network of veins (Plate 15b-f), all dominated by hydrated iron oxides (probably goethite). The iron oxides contain low levels of copper (up to 7 wt%, bulk 6%), zinc (up to 4 wt%, bulk 2%), arsenic (up to 0.8 wt%, bulk 0.6 wt%) and lead (up to 10 wt%, bulk 5wt%). Localised high concentrations of silver occur (Plate 15e; possibly as a sulphide), but bulk levels of silver are below 1 wt%.

Within the iron oxides, and cross-cut by some of the veins, are several grains of chalcopyrite up to 300 µm across (Plate 15f).

The late-stage green copper minerals on the outside of the fragment were not analysed.

DFC17/18: this sample comprised a collection of particles isolated from sample 125, hand-picked as appearing visually to be fragments of copper ore with either a green or a blue colour. The particles were divided to provide material for a bulk analysis (DFC17; ICP-MS only, comprising only particles with a blue colour), with four pieces (both green and blue in colour) mounted as a polished block for SEM examination (DFC18).

Particle 1: this particle appears at low magnification to be an amalgamation of small dark blue grains. The piece is approximately 8mm across.

In section the texture is complex, with blue, coarse-grained azurite, surrounding areas with a finer grain size and a dark blue-green colour (possibly malachite). The azurite is particularly well-developed around the margins of brown coloured enclaves, interpreted as pseudomorphic after siderite. The relict material in these enclaves shows angular, zoned crystal forms (Plate 16a; possibly still siderite in some cases), which have elevated arsenic contents (up to 4 wt%). These iron-rich grains are particularly well shown in the element map for iron (Plate 16b).

The azurite forms irregular grains about 500 µm across (Plate 16f), which locally enclose quartz grains. The azurite also shows intergrowths with radiating acicular crystals of mimetite (Plate 16e; lead chloro-arsenate, $Pb_5(AsO_4)_3Cl$).

Particle 2: this particle appears at low magnification to be formed of fine, green, laminae. The piece is approximately 8mm across and 2mm thick.

In section the piece can be seen to have a delicately botryoidal texture (Plate 17). Analyses show a composition that is very zinc-rich, with the copper content averaging 1.24 times that of zinc (on an atomic basis). This ratio suggests that the mineral is rosasite (Frost *et al*., 2007; a hydrated copper zinc carbonate with the formula $(Cu_{1-x},Zn_x)_2(CO_3)(OH)_2$ where x ranges between 0.3 and 0.5, in this case x=0.45).

Particle 3: this particle appears at low magnification to be an amalgamation of small green spheroids. The piece is approximately 7mm across.

In section this grain appears very similar to DFC16 particle 1 and DFC18 particle 1. The spheroids seen externally can be seen to be pseudomorphs of up to 400 µm formed by sheaves of elongate crystals of zincian malachite. The malachite shows a Cu:Zn ratio of 6.4 (i.e. a mineral where x=0.13, using the rosasite formula quoted above). Some grains are also marked by regions of silver enrichment in the form of dispersed tiny blebs. The interstitial areas are marked by quartz, which is often subhedral and occasionally euhedral. Pseudomorphs of probable siderite are seen as strongly facetted, zoned grains, up to 300 µm across (Plate 18a,c,d), with an elevated arsenic content (up to 4 wt%). The siderite pseudomorphs also contain low levels of copper (up to 4 wt%), zinc (up to 1.3 wt%) and lead (up to 5 wt%).

The exterior of the specimen shows some localised botryoidal overgrowths (Plate 18e) with a similar Cu:Zn ratio to the main development of malachite.

Particle 4: this particle appears at low magnification to be an amalgamation of small green spheroids. The piece is approximately 3mm across.

This piece has the same granular texture as particles 1 and 3. The malachite is slightly more zinc-rich than for particle 3, with a ratio of Cu:Zn of 4.74, corresponding to x=0.27 for the malachite/rosasite formula quoted above. This is at the upper limit of zinc substitution in zincian malachite reported by Behrens and Girgsdies (2010).

The section shows voids, some angular, filled by late botryoidal material, probably mainly mixed hydrated oxides, with up to 6 wt% manganese, 10wt% iron, 1.6 wt% cobalt, 8wt% copper, 4 wt% zinc 1 wt% arsenic and 5wt% lead.

There is a limited occurrence of grains of a silver-rich phase similar to that in DFC16 particle 1.

Chemical Composition of the samples

Bulk chemical compositions of the samples are presented in Tables 5 and 6.

The picked samples of azurite- and malachite-rich ores show some differences in composition, particularly the high levels of iron, lead, zinc, molybdenum and uranium in the malachite bearing ore. The rare earth element (REE) profiles (normalised to upper crust after Taylor and McLennan, 1981; Figure 2) of the two ore samples are similar, with flat profiles for the middle and heavy REE (with the azurite ore with slightly lower abundances than the malachite ore), but with depleted light REE (with slight superimposed negative Ce anomalies).

The lining samples show a fairly constant composition with 70wt% silica and 14-15wt% alumina and about 7wt% iron oxide. The zirconium content is rather high and in some samples niobium is also.

The various slag samples show, as would be expected, REE profiles of shape intermediate between the flat profiles, close to unity of the linings and the low, LREE-depleted profiles of the ores. The profiles are enriched compared with the ores because of removal of the metals during smelting. The ores similarly have high contents of uranium , molybdenum, chromium, cobalt and nickel.

In general, therefore, the slags show a chemical composition produced by simple mixing of ore and lining, modified by removal of the metallic elements into the copper and the volatilisation of zinc.

Interpretation

The nature of the ores

This study has provided some remarkable insight into the types of ore being smelted at Four Crosses. Before discussing this in more detail, it is important to remember that the total assemblage examined is extremely small (detailed analysis was undertaken on just seven grains), and it may suffer from some collecting bias. The ores are represented in the assemblage by two groups of material: firstly grains hand-picked from the 'slag' samples as being visually identifiable as ore and secondly grains contained within a mixed slag/ore assemblage extracted magnetically from sieved residues. The first group are dominantly pieces with green or blue colour (i.e. copper-rich), and thus easily identifiable, while the second group is limited to iron-rich materials that have been heated (either through roasting or through part-reaction in the smelting furnace) and thus had their magnetic properties enhanced. It is therefore possible that the original ore assemblage might have included other compositions not represented in the present material.

The ores examined can be divided into four types:

1. *azurite-dominated ore*: this type is represented by DFC18-p1. The azurite encloses zones which are interpreted as pseudomorphic after siderite, with relict material, possibly still siderite. The azurite grains frequently contained dispersed small blebs of a silver-rich phase (discussed further below). The azurite also shows intergrowths with radiating acicular crystals of mimetite (lead chloro-arsenate; $Pb_5(AsO_4)_3Cl$). Quartz (sometimes euhedral) occurs on the azurite grain boundaries and locally within the azurite grains.

observed assemblage:
azurite – quartz – siderite – mimetite – ?acanthite

2. *zincian malachite-dominated ore*: this ore type was seen in samples DFC16-p1, DFC18-p3, DFC18-p4. The malachite shows a high zinc content, with bulk Cu:Zn ratios of up to 4.7. The malachite encloses angular voids partially filled by zoned, angular crystals of siderite (as in the azurite ore above). The interstitial areas bear abundant grains of quartz, any of which show crystal facets. The sheaves of malachite crystals demark pseudomorphs of which the original mineralogy is uncertain. Given the overall similarity of the textures of these specimens to the azurite ores described above, it is possible the pseudomorphed mineral was azurite, rather than a primary phase.

observed assemblage:
zincian malachite – quartz – siderite – ?acanthite

3.*botryoidal rosasite ore:* this ore is represented by the single specimen DFC18-P2. The identification of rosasite, although likely, is tentative, being based solely on EDS analyses.

4. *reticulate iron-rich ores*: ore particles in this category include DFC4 grains 1 and 3 with DFC16-p2.

Grains 1 and 3 of DFC4 are heavily cracked, probably from dehydration of a hydrated mineral, most likely to have been goethite. They show strong similarities however to the fresh sample DFC16-p2. All three show even textured areas, probably indicating the original grains of the precursor rock, within a reticulated system of banded veins. In DFC-p2 there are a number of surviving grains of chalcopyrite. Several areas show localised silver enrichment. In DFC16-2 this is probably as a silver sulphide, but in DFC4 grain 1 the mineralogy is less certain and the silver may have been in an oxidised copper silver sulphide such as stromeyerite.

Although this material is dominated by iron, copper levels are high (at around 12 and 15 wt% in the two examples from DFC4 and 6 wt% in DFC16-2), zinc is present in lesser quantities (3 to 4 wt% in DFC4 and up to 4% in DFC16-2). Specimen DFC16-p2 also shows moderate levels of arsenic (<0.8 wt%).

5. *botryoidal/spherulitic iron-rich ores:* grain 2 of sample DFC4 possesses a spherulitic structure not seen in any other particle. The tentative interpretation of this structure is that it represents a dehydrated spherulitic growth of originally hydrated iron oxides, but it is possible that they were originally siderite. The oxides contain an external zone rich in tiny blebs rich in copper, zinc and lead (up to 6, 6 and 8 wt% respectively).

All of these ore classes are compatible with an origin in the supergene weathering of a primary ore body. The mineralisation on Llanymynech Hill is known to be of just such secondary mineralisation. The National Museum Wales, Mineralogy of Wales Database lists aurichalcite, azurite and malachite from the Llanymynech mines. The BGS Mineral Reconnaissance Report (BGS 1984) states "the veins... contain the ore minerals galena, sphalerite, chalcopyrite, pyrite, cerussite, calamine and malachite". Other sources for the ore are possible. The BGS report also notes, for instance, that "near Four Crosses [SJ 252 182, SH 257 175] two trials for haematite, one of which may contain a trace of copper, are recorded in the Ordovician shales".

The nature of the slags and other residues

The true slags comprise DFC4 grains 4 to 8, DFC5, DFC 6, and DFC14. DFC 7/8/9, DFC10/11, DFC12 and DFC13 are samples of vitrified furnace material.

The vitrified furnace material subjected to detailed analysis shows a thick layer with a high degree of vesicularity but with admixing of metallic materials only into the outer few millimetres. These features suggest that such vitrified clay may represent a single-use lining. The vitrified clay from other contexts was rather variable. The depth and extent of the vesicularity varied with some pieces of dense clay showing very little generation of vesicles. The dense clay was clearly a placed lining, and one well indurated, but not strongly vitrified, piece (from 2039) showed marks on the inner face from the smoothing of the wet clay.

Some of the most friable pieces of vitrified lining were from areas where any placed lining was thin, if present, and the vitrification resulted in the sintering of a gravelly sediment.

The vitrified material was almost all reduced –fired, but a small proportion was oxidised-fired. The oxidised material almost all showed rather specific features – such strongly convex morphology (2243), strongly folded internal lamination (2085), irregular vitrified surface possible from finger impressions (2229) or a 30° wedge-shaped section with the vitrification extending just around the acute angle onto a smooth, planar face (1769/1771). These features are suggestive of clay employed in the surround of the tuyère, with oxidation supplied by air leaking around the tuyère where it was not bonded well onto the surrounding clay.

Contexts 2245 and 2243 produced several sherds from block tuyères. At least 3 sherds are conjoining and are from the base of a tuyère. The form suggests 120mm wide block tuyère with a planar base and slightly rounded basal angles onto vertical sides. The base of the 25mm diameter bore lies 25mm above the base on the surviving, eroded, front face. The bore has a striated internal surface – presumably left by removal a (?wooden) former. The bore is inclined inwards at about 12° to the base of the tuyère. The front face of the tuyère overhangs by about 7°. Some less well-preserved sherds from 2243 may be from a second tuyère (or even possibly the upper part of the same tuyère), and suggest that the upper surface of the tuyère may have been curved, but this is far from certain.

The evaluation report suggested that some of the vitrified clay pieces may have had wattle impressions on the rear face. This has been reinterpreted as curved internal surfaces within a poorly-homogenised clay.

Many of the vitrified surfaces show adherent ferruginous or copper-rich dross. There are very few pieces of vitrified lining which show evidence for much movement of slag. The dense slag includes various blebs and small flow slag prills. These are indicative of a degree of slag movement within the charge, but the total amount of fluid slag was very small. The database shows (Table 2) just 855g of material identified as slag (excluding lining slags). Material sectioned for the analysis described here shows that some of this material is true flow slag, but some represents corroded copper prills. The amount of true slag per excavated furnace is therefore very small.

The rusty-appearing deposits of sintered ore and charcoal (see DFC14 above) are commonly seen both as individual particles (and accounted for in Table 2 within the copper slag) or as material attached to the lining (in which case they are included within the lining total). This material was formed by material descending to the floor, or attaching to the wall, of the furnace, usually with incomplete reaction.

Copper is present in the deposits as small corroded blebs and prills. Some of these are discrete bodies, but much of the copper surviving in the assemblage is present as inclusions within various slag materials.

The nature of the furnaces

The field evidence shows that the base of the furnaces was a pit 0.31 to 0.36m in diameter, lined with clay. The presence of furnace floor sinters and the copper attached to, and trapped within, the furnace lining, taken together with the complete lack of finds of crucibles on the site, indicate that this was not a crucible-based process. The clay may have been important to prevent loss of the copper formed in the reaction into the loose, gravel, substrate. The linings were dominantly reduced-fired, as would be expected in a pit furnace, and this may be one reason why the effects of heat were not always described by the excavators. Another reason may have been that the lining was deliberately removed at the end of a smelt, so that any trapped prills of copper could be retrieved.

The furnaces were blown through block tuyères, with a rectangular lower part – but just possibly a curved upper section. It is not known how many tuyères might have been employed in each furnace. Despite the presence of oxidised-fired clays which appear to be associated with the fastening of the tuyères into the structure, there is little clear indication of how they were positioned or oriented, although the downward angle of the bore in the preserved specimen would be appropriate for a tuyère block mounted horizontally. The wedge-shaped clay might indicate either clay covering the top of the tuyère (if the top was planar), or below the tuyère, if the tuyère projected into the furnace. If the tuyère did not project into the hearth, then the wedge of clay might represent a lip of the pit lining against the tuyère front, but this arrangement seems less likely.

There are no sections of fired clay with a clear outer surface – most appear to merge back into the gravelly subsoil. This suggests that most, if not all, of the vitrified clay recovered was employed as pit-lining, rather than as part of a superstructure. Some experimentalists have employed clay domes over copper smelting operations in order to aid the formation of suitably reducing conditions. The current evidence does provide supporting evidence. It might be expected that any such superstructure would tend to show external oxidised firing (although if sufficient organic temper is included this can be inhibited).

The high degree of vesicularity of the analysed lining requires further explanation. The vesicles must have been created by the release of a volatile material from the lining. Such volatile material is likely to have been either carbon dioxide (from decay of carbonate minerals or from combustion of organic matter) or water (from either a wet substrate or released from hydrated minerals). There is no evidence that the lining was lime-rich, so the explanation must either be that the lining was wet or organic-rich (or both). It is possible that the transformation of the lining into a frothy glass actually assisted with the trapping and subsequent retrievability of copper prills.

Discussion

The new evidence from Four Crosses allows a re-examination of the evidence from the "bowl-furnace", also of middle Iron Age date, found behind the rampart of the Llanymynech Hillfort (Musson & Northover 1989). This furnace was of similar size to the Four Crosses examples and contained residues with similar descriptions. It was interpreted as having been employed to smelt a sulphidic ore (thereby providing the iron included within the copper) in small-scale smelting within a crucible.

The petrographic details of the ores presented here, shows that at Four Crosses the ore was a mixture of various materials from the supergene oxidation zone, containing both copper-rich and iron-rich materials. The amount of sulphide mineral (chalcopyrite) appears very small in the examined specimens, but iron is present in both goethite and siderite. Both of these iron minerals also appears to contain considerable amounts of arsenic – another of the characteristic impurity elements in the Iron Age copper of North Wales. The main copper-bearing phase, is not a sulphide mineral, but the carbonate malachite (with lesser amounts of the carbonate azurite). The malachite has a very high proportion of zinc substitution – locally to the maximum apparently possible in zincian malachite, but with even higher levels present in rosasite. It is this zincian malachite which would be capable of supplying the high levels of zinc seen in some of the Iron Age copper from North Wales. At Four Crosses, however, the amount of zinc incorporated into the copper was not as high as has been reported elsewhere in the area in finds of raw copper (Northover 1991; Musson *et al.* 1992). The zinc must have been lost as vapour, or trapped in the iron-rich slags. Another of the characteristic impurities in copper in the Iron Age of North Wales is silver. Silver occurs in most of the ore specimens examined, either as native silver or as acanthite.

A single artefact from the Four Crosses site, a finger ring, shows on qualitative analysis to be a leaded bronze, with impurities of arsenic, silver and a little antimony. This artefact is probably to be added with the list of objects with the regional impurity signature, although it did not have detectable zinc. Indeed, so far as may be determined from the analysis, it matches the observed copper composition being produced at Four Crosses and may have been produced from copper smelted at this site.

Unfortunately, the great variability of both ores and slags means that a mass-balance description of the smelting reaction is not currently possible.

The copper smelting at Four Crosses thus satisfies the chemical requirements for a potential source of the regional copper source in the Middle Iron Age (Table 10), but does so using a technology (smelting in the furnace rather than within a crucible) and an ore (oxide/carbonate rather than sulphidic) that differs from that predicted by earlier work.

The technology employed might produce a rather inhomogeneous copper – with batches of ore capable of having rather different trace element suites depending on the precise mix used. Although the gathering of the prills and their possible remelting into larger cakes might reduce this effect within a smelt, some inhomogeneity might persist and might give rise to a variability in the copper composition between batches. Thus the regional copper may be characterised by a range of elemental impurities, rather than a very narrow range of possibilities.

References

BEHRENS, M & GIRGSDIES, F. 2010. Structural Effects of Cu/Zn Substitution in the Malachite–Rosasite System. *Zeitschrift für anorganische und allgemeine Chemie*, **636**, 919–927.

BGS 1984. *Regional geochemical and geophysical surveys in the Berwyn Dome and adjacent areas, North Wales*, Mineral Reconnaissance Report, No. 70.

FROST, R., WAIN, D., MARTENS, W. & REDDY, J. 2007. The molecular structure of selected minerals of the rosasite group - An XRD, SEM and infrared spectroscopic study. *Polyhedron,* **26,** 275-283.

MUSSON, C.R., BRITNELL, W.J., NORTHOVER, J.P. & SALTER, C.J. 1992. Excavations and metal-working at Llwyn Bryn-dinas Hillfort, Llangedwyn, Clwyd. *Proceedings of the Prehistoric Society*, **58**, 265-283.

MUSSON, C.R. & NORTHOVER, J.P. 1989. Llanymynech Hillfort, Powys and Shropshire: observations on construction work, 1981. *Montgomeryshire Collections*, **77**, 15-26.

NORTHOVER, J.P. 1991. Microfiche Appendix 13.4: Further comments on the composition of the Breiddin bronzes. *In:* C.R. Musson, *The Breiddin Hillfort: a later Prehistoric Settlement in the Welsh Marches*, London, Council for British Archaeology.

TAYLOR, S.R. & McLENNAN, S.M. 1981. The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philosophical Transactions of the Royal Society*, **A301**, 381-399.

YOUNG, T.P. 2006. Evaluation of archaeometallurgical residues from Four Crosses, Powys. *GeoArch Report 2006/11.* 3pp.

Mineral Glossary

Anglesite : lead sulphate, $PbSO_4$

Acanthite : a low T silver sulphide Ag_2S

Aurichalcite: : hydrated copper zinc carbonate, $(Zn,Cu)_5(CO_3)_2(OH)_6$

Azurite : hydrated copper carbonate, $Cu_3(CO_3)_2(OH)_2$

Barite : barium sulphate, $BaSO_4$

Calamine : an old name for either (1) zinc carbonate (smithsonite) $ZnCO_3$ or (2) zinc silicate (hemimorphite) $Zn_4Si_2O_7(OH)_2 \cdot H_2O$.

Cerussite : lead carbonate, $PbCO_3$

Chalcocite : copper sulphide, Cu_2S (artificial chalcocite is known as copper matte)

Chalcopyrite : iron copper sulphide, $CuFeS_2$

Cuprite : copper (I) oxide, Cu_2O

Delafossite: oxide of copper and iron, $CuFeO_2$

Fayalite: iron end-member olivine, Fe_2SiO4

Forsterite: magnesium end-member olivine, Mg_2SiO4

Franklinite : iron zinc spinel, $ZnFe_2O_4$ (artificial franklinite is also known as zinc ferrite)

Gahnite : zinc aluminium spinel, $ZnAl_2O_4$

Galena : lead sulphide, PbS

Goethite : a hydrated iron oxide, FeO.OH

Haematite : anhydrous iron (III) oxide, Fe_2O_3

Hemimorphite : zinc silicate, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$.

Hercynite : iron aluminium spinel, $FeAl_2O4$

Kirschsteinite : iron calcium olivine, $FeCaSiO_4$

Magnesioferrite : magnesium iron spinel, $MgFe_2O4$

Magnetite : iron spinel, Fe_3O_4

Malachite : hydrated copper carbonate $Cu_2(CO_3)(OH)_2$

Mimetite : lead chloro-arsenate, $Pb_5(AsO_4)_3Cl$

Monticellite : : magnesium calcium olivine, $MgCaSiO_4$

Olivine : a silicate mineral group including, amongst others, the end-members forsterite, fayalite, kirschsteinite and monticellite

Pyrrhotite : a non-stoichiometric iron sulphide, $Fe_{1-x}S$

Pyrite : an iron sulphide, FeS_2

Quartz : low temperature silica mineral, SiO_2

Rosasite : hydrated copper zinc carbonate with the formula $(Cu_{1-x},Zn_x)_2(CO_3)(OH)_2$ where $0.3 < x < 0.5$

Siderite : iron carbonate, $FeCO_3$

Smithsonite : zinc carbonate, $ZnCO_3$

Sphalerite : zinc sulphide, ZnS

Spinel: (1) an oxide mineral group including magnetite, hercynite, gahnite, franklinite, spinel (*sensu-stricto*) and magnesioferrite amongst others. (2) the magnesium aluminium spinel group mineral, $MgAl_2O_4$

Stromeyerite : a silver copper sulphide, AgCuS

Willemite : a zinc silicate, Zn_2SiO_4

Wustite : a non-stoichiometric iron oxide $Fe_{1-x}O$

Zincian malachite : hydrated copper zinc carbonate with the formula $(Cu_{1-x},Zn_x)_2(CO_3)(OH)_2$ where $x < 0.27$

Zincian wustite : an iron zinc oxide, $Fe_{1-x}Zn_xO$

Illustration Captions

Figure 1. Bivariate plots of zinc, arsenic and iron plotted against copper, all as weight% of EDS analysis of minerals. Left hand column shows data by sample, right hand column shows data by interpreted mineral phase.

Figure 2. Upper crust-normalised REE profiles of samples from Four Crosses

Plate 1
Backscattered electron photomicrographs: DFC1

a. area 1. Scale bar 4mm.
b. area 2. Scale bar 4mm.
c. area 3. Scale bar 200µm
d. area 4. Scale bar 300µm
e. area 5. Scale bar 40µm
f. area 6. Scale bar 200µm
g. area 7. Scale bar 300µm

Plate 2
Backscattered electron photomicrographs: DFC2

a. area 1. Scale bar 200µm
b. area 2. Scale bar 200µm
c. area 3. Scale bar 4mm
d. area 4. Scale bar 200µm

Plate 3
Backscattered electron photomicrographs: DFC3

a. area 1. Scale bar 4mm.
b. area 2. Scale bar 5mm.
c. area 3. Scale bar 100µm
d. area 4. Scale bar 200µm
e. area 5. Scale bar 200µm
f. area 6. Scale bar 200µm

Plate 4
Backscattered electron photomicrographs: DFC4

Montage of central area of mount (areas 5 to 11). Scale bar 3mm.

Plate 5
Backscattered electron photomicrographs: DFC4

a. area 1. Scale bar 1mm.
b. area 2. Scale bar 300µm.
c. area 3. Scale bar 1mm.
d. area 4. Scale bar 200µm.
e. area 12. Scale bar 300µm.
f. area 13. Scale bar 100µm.
g. area 14. Scale bar 200µm.
h. area 15. Scale bar 300µm.

Plate 6
Backscattered electron photomicrographs: DFC4

a. area 16. Scale bar 100µm.
b. area 17. Scale bar 400µm.
c. area 18. Scale bar 100µm.
d. area 19. Scale bar 400µm.
e. area 20. Scale bar 400µm.
f. area 21. Scale bar 800µm.
g. area 22. Scale bar 100µm.

Plate 7
Backscattered electron photomicrographs: DFC5

a. area 1. Scale bar 100µm.
b. area 2. Scale bar 100µm.
c. area 3. Scale bar 3mm.
d. area 4. Scale bar 100µm.
e. area 5. Scale bar 20µm.
f. area 6. Scale bar 100µm.
g. area 7. Scale bar 40µm.
h. area 8. Scale bar 40µm.

Plate 8
Backscattered electron photomicrographs: DFC5

a. area 9. Scale bar 80µm.
b. area 10. Scale bar 200µm.
c. area 11. Scale bar 100µm
d. area 12. Scale bar 80µm.

Plate 9
Backscattered electron photomicrographs: DFC6

a. area 1. Scale bar 100µm.
b. area 3. Scale bar 100µm
c. area 4. Scale bar 100µm.
d. area 5. Scale bar 100µm.
e. area 6. Scale bar 200µm.
f. area 7. Scale bar 100µm.
g. area 8. Scale bar 800µm.

Plate 10
Backscattered electron photomicrographs: DFC12

a. montage through specimen. Areas 1-10. Scale bar 100mm.
b. area 15. Scale bar 70µm.
c. area 14. Scale bar 100µm.
d. area 13. Scale bar 100µm.
e. area 12. Scale bar 100µm.
f. area 11. Scale bar 100µm.

Plate 11
Backscattered electron photomicrographs: DFC12

a. area 16. Scale bar 1mm.
b. area 17. Scale bar 400µm.
c. area 18. Scale bar 300µm.
d. area 19. Scale bar 30µm.

Plate 12
Backscattered electron photomicrographs: DFC13

a. area 1. Scale bar 1mm.
b. area 2. Scale bar 200µm.
c. area 3. Scale bar 1mm.
d. area 4. Scale bar 300µm.

Plate 13
Backscattered electron photomicrographs: DFC14

a. area 1. Scale bar 1mm.
b. area 2. Scale bar 600µm.
c. area 3. Scale bar 4mm.
d. area 4. Scale bar 2mm.

Plate 14
Backscattered electron photomicrographs: DFC16-p1

a. area 1. Scale bar 600µm.
b. area 6. Scale bar 400µm.
c. area 7. Scale bar 60µm.
d. area 8. Scale bar 1mm.
e. area 9. Scale bar 200µm.
f. area 10. Scale bar 90µm.

Plate 15
Backscattered electron photomicrographs: DFC16-p2

a. area 2. Scale bar 5mm.
b. area 3. Scale bar 1mm.
c. area 4. Scale bar 1mm.
d. area 5. Scale bar 1mm.
e. area 11. Scale bar 300µm.
f. area 12. Scale bar 300µm.

Plate 16
Backscattered electron photomicrographs and element maps: DFC18-p1

a. area 5. BSEM image. Scale bar 600µm.
b. area 5. Element map for iron.
c. area 5. Element map for copper.
d. area 5. Element map for silicon.
e. area 7. Scale bar 200µm.
f. area 8. Scale bar 500µm.

Plate 17
Backscattered electron photomicrographs: DFC18-p2

a. area 9. Scale bar 1mm.
b. area 4. Scale bar 1mm.

Plate 18
Backscattered electron photomicrographs: DFC18-p3

a. area 1. Scale bar 600µm.
b. area 2. Scale bar 1mm.
c. area 3. Scale bar 200µm.
d. area 10. Scale bar 600µm.
e. area 11. Scale bar 600µm.

Plate 19
Backscattered electron photomicrographs: DFC18-p4

a. area 6. Scale bar 600µm.
b. area 12. Scale bar 400µm.

Table 1: summary catalogue

Context	***Context notes***	***Sample label***	***Weight g***	***Notes***
1767	Final fill of 1766	slag	108.4	slag
1767	Final fill of 1766	Cu	0.0	Cu drops
1769/1771	Same as 1767	Cu	0.3	Cu drops
1769/1771	Same as 1767	slag/kiln lining	628.0	fired clay assemblage more oxidised than 2299. Some complex pieces show a 30 degree wedge shaped section with the vitrification just reaching onto the flat face. Maybe part of the tuyère mounting?
1798	Final fill of 1796	slag	538.0	collection of dominantly reduced-fired material, generally gravelly, with a well vitrified surface, often overlain by dross with abundant Cu debris.
1798	Final fill of 1796	Cu	0.0	Cu bits
1798	Final fill of 1796	Cu	6.3	Cu slag
1798	Final fill of 1796	magnetic material	0.3	slag, sphere, Cu-slag
2039	Primary fill of 2034	magnetic material	0.9	abundant Cu slag debris
2039	Primary fill of 2034	Cu	2.9	Cu drops
2039	Primary fill of 2034		24.2	dense Cu slags
2039	Primary fill of 2034		10.1	slab of fired but not vitrified lining (true lining) from inside furnace, smoothing marks on one side, with a copper bleb, c5mm thick; second piece is fired but vitrified piece of grey gravelly ceramic
2048	Same as 2039	furnace lining	2.6	2 scraps of lining, one harder piece - not certain if clay pebble or from tuyère
2048	Same as 2039	magnetic material	0.8	abundant Cu slag
2048	Same as 2039	Cu	1.5	Cu drops
2048	Same as 2039	slag/copper slag	88.3	dense Cu slags
2057	Same as 2039		1.2	abundant Cu slag
2057	Same as 2039	Cu	4.4	Cu drops
2057	Same as 2039		85.5	dense Cu slags
2060	Same as 2039	furnace lining	0.6	
2060	Same as 2039	magnetic material	0.7	abundant Cu-slag
2060	Same as 2039	Cu	1.2	Cu drops
2060	Same as 2039		59.5	dense Cu slags
2072	Final fill of 2071	magnetic material	0.5	abundant Cu slag
2072	Final fill of 2071	slag	4.2	black glassy slag - quite dense
2072	Final fill of 2071	Cu	0.2	Cu bits
2072	Final fill of 2071		89.5	dense Cu slags
2072	Final fill of 2071	furnace lining	292.0	mixture of small pieces of unvitrified reduced-fired clay and large blocks with lots of dark glass with indicators for down-wall flowage. 1 curious nub has a hole and peripheral oxidised firing, but probably not a tuyère.
2085	Same as 2072	magnetic material	0.6	abundant Cu slag
2085	Same as 2072	Cu	0.2	Cu drops
2085	Same as 2072		45.7	dense Cu slags
2085	Same as 2072	slag	186.4	similar to 2283 mainly - lots of damage to wall, probably in over blowhole area. 1 piece shows oxidised fired laminated prepared clay and is probably very close to blowhole.
2090	Primary fill of 2071	furnace lining	840.0	mainly rather lowly fired clay with natural backs and slightly grey surface. Not much vitrification on this batch and no real sign of prepared ceramics
2212	Secondary fill of 2210	slag	16.5	abundant Cu slag with slag spheres.
2212	Secondary fill of 2210	Cu	0.9	Cu drops
2212	Secondary fill of 2210	magnetic material	0.5	dense Cu slags
2213	Final fill of 2210	fired clay?	3.0	highly vitrified lining
2213	Final fill of 2210	copper\slag	8.8	4 small pieces of the ferruginous hearth sediment, one rounded bleb of brown slag but now is 6 pieces
2213	Final fill of 2210	magnetic material	1.1	abundant Cu-slag - includes spheres
2213	Final fill of 2210	Cu	0.2	Cu drops
2213	Final fill of 2210		51.2	dense Cu slags
2220	Primary fill of 2219	magnetic material	1.8	abundant Cu slag

Context	*Context notes*	*Sample label*	*Weight*	*Notes*
2220	Primary fill of 2219	copper	0.4	Cu drops
2220	Primary fill of 2219	copper slag	1.4	Cu slags plus small piece of possible blue ore
2229	Same as 2220	furnace lining	10.8	vitrified clay and charcoal
2229		magnetic material	0.2	abundant Cu-slag
2229	Same as 2220	slag, 1 x frag for xrf	114.0	analysed fragment is similar to gravelly reddened material from other collections - but has very smooth striated face- could be tuyère margin. The other pieces are the reduced-fired porous gravelly glass seen in the other collections. Some pieces have Cu spheres attached
2229		fired clay	10.6	reddened fired clay, very irregular face (finger presses?) with attached Cu dross, flat "base" (pressed against tuyère ?)
2229	Same as 2220	copper	1.4	Cu drops
2229	Same as 2220	slag/copper slag	9.0	dense Cu slags
2243	Primary fill of 2242	furnace lining/slag	92.4	3 pieces of more standard vitrified material on gravelly lining, 1 piece of dense dross from hearth floor. 5 pieces of probable tuyère with well burnt back top
2243	Primary fill of 2242	magnetic material	4.4	abundant slag
2243	Primary fill of 2242	cbm	152.4	conjoining piece of tuyère. bore angled at 12 degrees to base. Front face overhangs by about 7 degrees . Striated bore, clay well indurated, fine, possible base to piece is planar surface. Small fragment (6g) from same block occurs in 178g, and large block (110g) in 2245.
2243	Primary fill of 2242	copper	0.0	Cu drops
2243	Primary fill of 2242	slag	1.7	dense Cu slags, 2 pieces
2243	Primary fill of 2242	fired clay	178.4	mainly small fragments of the usual gravelly vitrified clay. 3 small pieces of ferruginous dross with charcoal. 1 small piece (6g) is spalled from the curved corner of the oxidised tuyère fragment from 2245. Another fragment has maroon indurate fired clay and is probably from the same block.
2245	Same as 2243	fired clay	110.0	1 piece of sintered friable reduced basal material with vitrified surface, 1 piece of oxidised fired prepared tuyère block (85g) (adjoins material from 2243 (*) above) [probably the block that went to DD, but not labelled]
2245	Same as 2243	magnetic material	1.2	abundant Cu slag
2245	Same as 2243	copper4	0.3	Cu drops
2245	Same as 2243		25.1	dense Cu slags
2245	Same as 2243	furnace lining slag	8.0	the piece from this bag went to DD. Purple at base of thick vitrified layer- usual fabric. Highly vesicular lining
2253	Primary fill of 2252	magnetic material	0.4	abundant Cu slag
2253	Primary fill of 2252		8.8	dense Cu slags
2253	Primary fill of 2252	furnace lining	22.3	small pieces of usual gravelly ceramic with vitrified surface
2253	Primary fill of 2252	slag	8.3	vitrified stone and gravelly lining
2254	Same as 2252	magnetic material	0.4	abundant Cu-slag debris
2254	Same as 2252	Cu	0.1	Cu droplets
2254	Same as 2252	slag	34.4	small number of fragments of friable grey gravelly fired clay with Cu material in crevices
2254	Same as 2252	furnace lining		vitrified lining, lining slag, Cu-slag blebs
2258	Primary fill of 2257	magnetic material	0.1	
2258	Primary fill of 2257	slag	4.4	vitrified gravelly clay
2259	Same as 2257	magnetic material	0.1	
2259	Same as 2257		0.3	brown glassy copper slag fragment
2273	Primary fill of 2272	magnetic material	1.1	abundant Cu slag
2273	Primary fill of 2272	Cu	0.9	Cu drops
2273	Primary fill of 2272	fired clay	1183.4	variable collection of fired clay. Much is reduced-fired sintered gravelly material with a superficial vitrified layer, often with Cu residues. A few pieces show formed clay with an organic temper, these are oxidised fired on curved surfaces
2274	Same as 2273	burnt stone	31.6	
2274	Same as 2273	magnetic material	1.0	abundant Cu slag
2274	Same as 2273	Cu	1.0	Cu drops
2274	Same as 2273		0.4	small glassy slag piece
2282	Primary fill of 2281	fired clay	198.0	two or three small fragments of possible tuyère margin or other prepared clay. Bits of vitrified surface, 1 large chunk of vitrified gravelly wall. 2 pieces of black resiny-looking slag with signs of having been stretched
2282	Primary fill of 2281	Cu	0.5	Cu drops
2282	Primary fill of 2281	magnetic material	0.5	dense Cu slags
2282	Primary fill of 2281		8.8	slag

Context	***Context notes***	***Sample label***	***Weight***	***Notes***
2283	Same as 2282	Cu	0.1	Cu drops
2283	Same as 2282		0.3	Cu slag
2283	Same as 2282	hammer scale	< 0.01	one spheroid of slag
2283	Same as 2282		3.8	dense Cu slags
2283	Same as 2282	furnace lining	301.4	probably originally a single slab of highly vitrified wall from around the blowhole area. Elongate vesicles and lobes indicate down wall slag flowage. Lots of evidence for weathered Cu material
2291	Primary fill of 2290	furnace lining	34.0	broken slab of grey wall with thick vitrified layer, lilac at base
2292	Same as 2291	fired clay?	0.7	vitrified lining from Cu hearth
2291	Primary fill of 2290	magnetic material	0.1	slag
2292	Same as 2291	magnetic material	0.1	slag
2298	Primary fill of 2297		152.4	slag
2299	Same as 2298		39.1	slag
2298	Primary fill of 2297	fired clay	512.4	a collection of very hard reduced fired material with strongly vitrified surfaces. These look like prepared clay - possibly as a hearth lining. Very indurated and has lilac tint below vesicular layer
2299	Same as 2298	magnetic material	0.1	dense Cu slags
2299	Same as 2298	fired clay	1347.4	difficult assemblage varying from unfired material all the way to glass. No diagnostic Cu-alloy colours. Some Curved surfaces suggest blowhole but very close to face -so may be wattle, Other pieces are dish shaped with vitrification dying onto flat - so may be from base of hearth walls?
2314	Primary fill of 2313	fired clay	98.3	small fragments of fired and vitrified clay, a few pieces of ferruginous drossy material, 1 piece of Curved fired clay - could be corner of a tuyère block but not very dense.
2314	Primary fill of 2313	magnetic material	1.0	abundant slag
2315	Same as 2314	fired clay	90.4	1 piece shows fine clay with partially oxidised firing, Curved internal structure to clay running into planar surface - so probably the edge of pre-fabricated piece - presumably a tuyère, or they clay pressed against the tuyère? The surface is deeply vitrified and coated in a black glass. The other major piece is a slab of gravelly material, deeply vitrified, with a pronounced convex shape.
2315	Same as 2314	magnetic material	0.6	abundant slag
2315	Same as 2314	Cu	0.2	Cu drops
2374	Primary fill of 2373	Cu	0.3	Cu drops
2374	Primary fill of 2373		13.7	dense Cu slags
2374	Primary fill of 2373	magnetic material	0.4	
2374	Primary fill of 2373	fired clay	158.4	large slab of vitrified surface on normal wall - possibly leaving wall to arch across a gap onto ?floor. Lots of small fragments probably associated. 1 piece shows strong Cu-oxide colouration
2375	Same as 2374	magnetic material	1.8	abundant Cu slag
2375	Same as 2374	fired clay	672.4	amorphous and sheet-like material from fired clay lining (and gravel substrate) of Cu-alloy working hearth. Clay with strong fabric and well broken up - fired wet? Large pieces are good vitrified wall. Some accumulations of weathered Cu spheroids. One piece shows lining turning lilac below, so fractionation of oxides is occurring. Lining almost entirely reduced fired.
2375	Same as 2374	Cu	0.4	Cu drops
2375	Same as 2374		1.2	dense Cu slags

Table 2: distribution of residue classes by feature, using initial identifications from evaluation report.

			magnetic material	lining	tuyère	Cu slag	Cu drops	***total residue***
Feature 1766								
	1767	final				108	0.0	***108***
	1769/1771	primary		628			0.3	***628***
Feature 1796								
	1798	final	0.3	538		6	0.0	***545***
Feature 2034								
	2039/2048/2057/2060	primary	2.3	13		259	10.0	***284***
Feature 2071								
	2072/2085	final	1.1	478		139	0.2	***619***
	2090	primary		840			0.2	***840***
Feature 2210								
	2212	secondary	0.5			22	0.9	***23***
	2213	final	1.1	3		60	0.2	***64***
Feature 2219								
	2220/2229	primary	2.0	136		12	1.8	***152***
Feature 2242								
	2243/2245	primary	5.6	350	243	27	0.3	***626***
Feature 2252								
	2253/2254	primary	0.7	65		17	0.1	***83***
Feature 2257								
	2258/2259	primary	0.2	4		0	0.0	***5***
Feature 2272								
	2273/2274	primary	2.1	1215		0	1.9	***1219***
Feature 2281								
	2283/2284	primary	0.8	499		13	0.6	***513***
Feature 2290								
	2291/2292	primary	0.1	35				***35***
Feature 2297								
	2298/2299	primary	0.1	1860		191		***2051***
Feature 2313								
	2314/2315	primary	1.5	189			0.2	***190***
Feature 2373								
	2374/2375	primary	2.1	831		22	0.7	***856***
			18.4	***6853***	***243***	***855***	***16.8***	***7987***

Table 3: material sampled for analysis

sample	material	c	s		XRF	ICP-MS	SEM
DFC1	copper	2212	122	secondary fill of 2210			X
DFC2	copper	2229	126	primary fill of 2219			X
DFC3	copper	2374	156	primary fill of 2373			X
DFC4	magnetic fines	2243	127	primary fill of 2242		X	X
DFC5	flow slag	2243	127	primary fill of 2242	X	X	X
DFC6	flow slag	2048	106	primary fill of 2034	X	X	X
DFC7	lining	2243	furnace lining	primary fill of 2242			X
DFC8	lining	2243	furnace lining	primary fill of 2242	X	X	
DFC9	lining	2243	furnace lining	primary fill of 2242	X	X	
DFC10	lining	2229	furnace lining	primary fill of 2219	X	X	
DFC11	lining	2229	furnace lining	primary fill of 2219	X	X	
DFC12	lining	2229	furnace lining	primary fill of 2219			X
DFC13	lining	2229	furnace lining	primary fill of 2219			X
DFC14	Fe-rich "sinter"	2243	copper slag	primary fill of 2242	X	X	X
DFC15	Fe-rich malachite ore	2229	126 (slag)	primary fill of 2219		X	
DFC16	ore	2229	126 (slag)	primary fill of 2219			X
DFC17	azurite	2220	125 (slag)	primary fill of 2219		X	
DFC18	ore	2220	125 (slag)	primary fill of 2219			X

Table 4: Possible metallurgical features

Cut	primary	secondary	final	notes	E	N	samples								
1766	1769/1771		1767	pit 0.52m diameter, 0.18m, not burnt, primary charcoal rich fill on W side, NE edge of interior of ringditch	7107	8719									
1796			1798	pit 0.32d x 0.12m, scorched sides - sloping out so may be larger, truncated, abuts 1766	7106	8719									
2034	2039=2048=2060=2057			pit 0.36d x 0.12, possible grey clay lining	6990	8780	DFC6								
2071	2090		2072=2085	pit 0.31 x 0.11m, fired clay lining 2090 - lining is thick 30-60mm and shallow suggesting highly truncated?	6990	8780									
2210		2212	2213	pit 0.33d x 0.09m, lower charcoal rich fill	7040	8740	DFC1								
2219	2220=2229			pit 0.70x0.32 x 0.17deep, primary charcoal rich fill particularly in deep end	7030	8740	DFC2	DFC10	DFC11	DFC12	DFC13	DFC15	DFC16	DFC17	DFC18
2242	2243=2245			pit 0.31d x 0.19deep, lower fill interpreted as in-situ burning, deep charcoal and slag rich fill	7030	8740	DFC4	DFC5	DFC7	DFC8	DFC9	DFC14			
2252	2253=2254			pit 0.16m diameter, 0.12 deep	7030	8740									
2257	2258=2259			pit 0.40 x 0.48, x0.30m deep, simple fill with single slag piece - so weaker evidence	7030	8740									
2272	2273=2274			pit 0.36m diameter, 0.19 deep, Cut faces burnt, may have stone base, large pieces of lining	7040	8740									
2281	2282=2283			sub square pit 0.28x0.33 x 0.15 deep, very charcoal rich fill	7040	8740									
2290	2291=2292			0.23m d x 0.05m deep, charcoal and slag fill, lies alongside 2297 and 2281	7040	8740									
2297	2298=2299			sub square pit 0.25x0.23 x 0.09 deep, very charcoal rich fill, possible in situ fired lining on S side, charcoal layer on base	7040	8740									
2313	2314=2315			pit 0.28x0.34x0.12, with charcoal and slag rich fill	7040	8740									
2373	2374=2375			pit 0.32x0.6x0.08, in situ fired lining in E end hints at more regular circular pit	7030	8740	DFC3								

Table 5: Chemical analyses by XRF.

5a – major elements as wt% oxides

		SiO_2	Al_2O3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K2O	TiO_2	P_2O_5	LOI	LOI	Total
DFC 5	Flow slag	17.60	5.37	54.97	49.47	0.18	2.47	5.81	0.38	0.80	0.29	0.19	-3.04	2.46	99.94
DFC 6	Flow slag	28.48	2.92	33.05	29.74	0.20	1.47	3.91	0.57	0.70	0.22	0.60	-2.02	1.28	99.40
DFC 8	Inner wall	68.99	14.92	7.34	6.60	0.17	1.35	0.09	1.12	2.33	1.02	0.58	0.85	1.58	100.31
DFC 9	Outer wall	68.98	14.28	9.17	8.26	0.17	1.40	0.39	1.21	2.83	0.96	0.50	-0.08	0.83	94.84
DFC 10	Inner wall	71.19	14.69	6.99	6.29	0.19	1.31	0.35	1.11	2.38	0.94	0.70	1.06	1.76	101.03
DFC 11	Outer wall	70.46	15.00	7.04	6.34	0.15	1.26	0.79	1.16	2.90	0.99	0.58	-0.39	0.32	101.68
DFC 14	Sinter	10.83	2.67	39.18	35.26	0.11	1.69	0.41	0.20	0.24	0.17	0.32	16.97	20.89	100.72

5b – trace elements as wt% oxides

		SO_3	V_2O_5	Cr_2O_3	SrO	ZrO_2	BaO	NiO	CuO	ZnO	PbO
DFC 5	Flow slag	0.42	0.02	0.01	0.02	0.04	2.03	0.01	2.62	8.89	0.11
DFC 6	Flow slag	0.18	0.02	0.02	0.01	0.04	0.02	0.11	6.90	18.89	2.85
DFC 8	Inner wall	0.09	0.02	0.01	0.01	0.08	0.04	0.01	0.05	0.13	0.03
DFC 9	Outer wall	0.09	0.02	0.01	0.02	0.07	0.07	0.01	1.12	0.61	0.03
DFC 10	Inner wall	0.09	0.02	0.01	0.02	0.07	0.03	0.02	0.14	0.04	0.03
DFC 11	Outer wall	0.12	0.02	0.01	0.02	0.07	0.04	0.03	1.24	0.09	0.06
DFC 14	Sinter	0.42	0.01	0.01	0.02	0.03	2.24	0.06	24.20	0.19	0.17

Table 6a Chemical analysis of major elements by ICP-MS expressed in wt% oxides.

	MnO	Fe_2O_3	TiO_2	P_2O_5
DFC4	0.15	65.05	0.21	0.81
DFC5	0.15	54.98	0.30	0.10
DFC6	0.18	32.05	0.18	0.06
DFC8	0.14	6.70	0.93	0.59
DFC9	0.13	8.28	0.84	0.40
DFC10	0.15	5.68	0.70	0.57
DFC11	0.13	7.02	0.99	0.54
DFC14	0.09	37.81	0.18	0.10
DFC15	0.04	40.88	0.06	0.01
DFC17	0.01	1.48	0.05	0.00

Table 6b. Chemical analyses of trace elements by ICP-MS, expressed in ppm.

	Sc	V	Cr	Co	Ni	Ga	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba
DFC4	4.62	47.26	72.37	100.67	865.1	14.40	15.50	27.88	11.98	98.31	3.89	73.94	1.26	1.16	529
DFC5	6.30	60.31	69.44	136.00	243.8	18.41	22.77	120.26	25.89	137.47	6.08	96.30	1.82	1.02	9195
DFC6	5.25	99.95	108.40	771.01	1036.3	20.69	20.95	35.69	31.48	110.82	11.61	237.30	3.81	4.62	227
DFC8	11.57	96.86	75.95	16.54	108.4	19.68	111.11	71.84	27.95	300.67	15.42	0.65	6.12	5.34	384
DFC9	10.93	79.29	70.70	21.20	125.0	16.89	102.84	74.80	26.07	274.69	148.75	7.03	3.76	5.11	594
DFC10	8.72	68.73	59.14	17.65	244.5	15.18	83.35	62.95	21.21	221.04	10.79	1.20	4.22	3.31	295
DFC11	13.93	98.64	73.26	38.98	137.6	18.69	134.39	92.32	29.28	334.91	198.35	26.40	6.10	7.94	511
DFC14	3.89	51.78	78.04	67.52	651.7	23.55	9.99	54.55	13.10	121.96	5.52	82.13	3.03	0.53	9815
DFC15	1.86	23.44	36.16	33.79	1162.8	12.24	5.07	15.84	10.65	74.62	1.43	111.15	1.54	1.35	80
DFC17	1.97	6.44	13.50	50.74	2505.1	1.08	5.45	9.70	5.59	73.50	1.35	30.56	2.33	1.94	65

Table 6b. Chemical analyses of trace elements by ICP-MS, expressed in ppm.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Th	U
DFC4	6.781	13.605	1.866	7.407	1.668	0.385	1.524	0.247	1.709	0.339	0.964	0.142	0.843	0.131	2.733	0.533	2.50	56.42
DFC5	12.821	24.484	3.679	14.381	3.179	0.828	3.216	0.494	3.395	0.661	1.913	0.276	1.633	0.242	3.597	0.457	4.11	87.48
DFC6	12.931	17.984	4.161	17.095	3.656	0.876	3.637	0.538	3.634	0.721	2.051	0.292	1.732	0.269	2.911	3.929	3.53	118.72
DFC8	39.281	77.790	8.841	30.663	5.430	1.013	4.507	0.708	4.569	0.888	2.651	0.431	2.808	0.442	8.074	1.204	9.70	2.62
DFC9	33.044	67.878	7.907	27.779	5.006	0.970	4.194	0.633	4.160	0.801	2.453	0.391	2.541	0.402	7.353	58.065	8.88	6.96
DFC10	28.873	59.361	7.088	25.087	4.696	0.876	3.796	0.544	3.589	0.671	2.109	0.336	2.198	0.344	6.099	0.905	7.67	2.06
DFC11	40.111	82.741	9.752	34.306	6.211	1.215	5.216	0.747	4.798	0.924	2.872	0.452	3.045	0.468	8.843	69.796	10.35	3.75
DFC14	8.723	16.126	2.485	9.861	2.343	0.499	2.113	0.330	2.218	0.421	1.202	0.177	1.013	0.160	3.095	0.906	2.38	77.48
DFC15	3.026	5.963	1.156	5.124	1.419	0.371	1.485	0.253	1.721	0.340	0.930	0.136	0.782	0.120	2.101	0.144	0.70	45.44
DFC17	3.096	7.065	1.307	5.800	1.458	0.326	1.061	0.168	1.027	0.194	0.554	0.094	0.648	0.107	2.010	0.109	0.39	1.59

Table 7: Archive EDS microanalytical data expressed as wt% element. All elements analysed. For locations see plates. < = below detection.

DFC	area	#	type	prov. phase	wt% O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
1	3	1	area	copper	1.31			0.40			1.66											96.70	<	0.73									100.80
1	3	2	point	copper	0.80			0.48														98.82	<	0.87									100.97
1	3	3	point	copper	0.88			0.48													0.31	98.28	<										99.95
1	3	4	point	sulphide	8.75			<	<		11.33								3.37			42.29	33.51										99.27
1	3	5	point	copper	0.68			0.27														94.43	<	2.43				0.79		0.37			98.97
1	4	1	area	copper	1.30			0.26	<		1.82											99.44	0.56	0.78									104.16
1	5	1	point	copper	0.92			0.46														100.32	<	<									101.70
1	5	2	point	sulphide	0.57						20.62											80.39	<										101.58
1	5	3	point	sulphide	0.52						20.40											80.71	<									1.35	102.98
1	6	1	point	copper	0.92			0.39														97.55		0.44									99.31
1	6	2	area	copper	1.31			0.36			1.76											94.87		1.07									99.36
1	7	1	area	copper	1.65			0.31			1.69	0.15										95.24		0.88				0.43					100.35
2	4	1	area	copper	1.79			0.49			0.32								0.39		0.54	95.42		1.32				0.37				2.23	102.87
3	4	1	area	copper	2.41			0.54			0.51	0.19							1.20		0.35	91.02		0.74				0.29				2.05	99.29
3	5	1	area	copper	2.82			0.50			0.50								1.54		0.43	90.97		0.74				0.25				1.98	99.71
3	6	1	area	copper	2.10			0.39			0.44	0.31							0.54		0.26	93.76		0.95								3.05	101.80
3	6	2	point	lead	9.15			0.34			<	10.64										40.71		9.29								38.04	108.17
3	6	3	point	sulpide	0.74			<			18.72											74.50											93.96
3	6	4	point	copper	0.68			0.23											0.52		0.37	95.83											97.62
3	6	5	point	sulpide	1.69			<			18.72											76.77						1.76				1.61	100.55
3	6	6	point	lead	9.38			0.17				10.38										4.85						<				73.69	98.47
4	2	1	area	copper b	2.06			0.53	<		0.30								0.67			97.14	0.89										101.59
4	2	2	area	copper	4.48		<	0.62	0.29		0.19								2.46			87.14	0.93										96.10
4	2	3	area	copper	1.26		<	0.53	<		0.23								2.60			95.82	0.88	0.53									101.85
4	2	4	area	copper	1.13		<	0.54	<		0.22								2.95			97.01	0.66					0.39					102.90
4	2	5	point	copper	1.07		<	0.35	<		0.18								2.78			99.31	0.97										104.66
4	2	6	point	copper	1.30			0.70	<										2.08		0.35	96.79	1.15										102.37
4	2	7	point	copper	1.43				<		0.31								2.88			93.90	0.74	<									99.27
4	2	8	point	copper	1.27			0.52	<		<								2.48			94.84	0.95										100.05
4	2	9	point	copper	1.13			0.58	<										4.67			93.42	1.05					0.41					101.24
4	2	10	point	copper	1.45			0.63			0.18								4.41			91.37	0.99										99.04
4	2	11	point	magnetite	27.95			2.89	0.63						0.17				60.86				6.96										99.45
4	2	12	point	olivine?	29.48		2.84	<	14.43					0.29				0.31	42.79				10.17										100.30
4	2	13	point	copper	7.89			0.75	0.12		0.18	0.15							3.31			86.36	0.37										99.15
4	2	14	point	olivine?	28.87		2.45	0.13	13.64					0.39				0.19	40.76				9.37										95.79
4	2	15	point	glass / olivine	32.98			4.34	17.50	0.18	<		3.54	4.04					21.76				10.79								3.23		98.36
4	2	16	point	glass / olivine?	34.04		0.39	3.86	17.38	0.16			3.31	2.01					29.32			0.54	9.70								1.73		102.44
4	2	17	point	glass / olivine?	33.02			4.49	17.85	0.21			3.60	4.23					21.26				10.94								3.14		98.73
4	2	18	point	magnetite	25.89		0.30	6.83	0.23						0.90				53.58			0.43	9.31										97.48
4	2	19	point	olivine?	29.44		2.65		14.30					0.30				0.23	42.52				9.78										99.23
4	2	20	point	olivine?	29.05		2.91		14.16					0.27				0.26	42.22				9.83										98.71
4	2	21	point	magnetite	27.11			6.14	0.21						0.64				55.46				9.16										98.71

DFC	area	#	type	prov. phase	wt%																												
					O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
4	4	1	point	glass	34.29		1.22	0.99	18.04	0.20			1.21	11.60					10.98			1.62	19.55								3.68		103.39
4	4	2	point	copper	1.44			0.52	<		<								2.33			102.28	<	1.21									107.78
4	4	3	point	copper	1.45				<		<								2.36			100.70	<	0.98									105.50
4	4	4	point	copper	2.03			0.53	<										2.27			100.60	<										105.43
4	4	5	point	copper	1.70			0.70	<										3.19			99.77	<										105.37
4	4	6	point	copper	1.48			0.63	<										3.88			102.88	<										108.88
4	4	7	point	copper	1.43			0.59	<										4.46			101.69	<										108.17
4	4	8	point	glass	34.05		1.27	1.09	19.10	0.19			1.57	11.31					8.80			4.33	17.24								3.39	0.94	103.28
4	4	9	point	magnetite	26.72		1.11	0.99							0.17				56.35			0.46	18.90										104.70
4	4	10	point	magnetite	25.77		1.28	0.89											57.29			1.02	17.50										103.76
4	12	1	point	metallic bleb	1.86				0.28		12.61								14.88			25.88						39.20				1.71	96.41
4	12	2	point	Fe-oxide	25.40				2.17			0.26							52.96			12.50	1.86										95.15
4	12	3	point	Fe-oxide	20.87			0.44	0.74			0.17							49.76			12.16	3.73							0.40			88.28
4	13	1	area	Fe-oxide	24.36			0.58	3.54					0.50					57.46			2.35	5.18									0.58	94.55
4	13	2	point	Fe-oxide	24.17				2.91					0.73					56.07			5.68	5.58	<								8.18	103.32
4	13	3	point	Fe-oxide	27.16			0.18	3.96				0.13	2.17					58.90				4.86									0.57	97.93
4	13	4	point	Fe-oxide	24.58				3.54					0.25					62.41			0.63	4.66										96.08
4	14	1	point	Fe-oxide	20.65				0.72	0.15									57.97			0.46	3.01										82.97
4	14	2	point	Fe-oxide	24.65				4.14		0.40			0.68					48.00			11.01	2.16									0.87	91.91
4	14	3	point	Fe-oxide	22.50				1.62					0.21					49.43			15.28	2.51										91.56
4	14	4	point	Fe-oxide	29.29				4.60		0.38			0.97					57.23			2.80	2.53									0.86	98.65
4	14	5	area	Fe-oxide	20.78			0.35	2.16		0.17			0.34					43.52			12.07	2.11									0.54	82.05
4	16	1	area	bulks	32.93		0.84	5.99	15.64				2.26	0.87	0.28				33.35			3.95											96.09
4	16	2	area	bulk	20.86		0.91	3.00	3.46				0.30	0.29	0.20				33.82			21.12											83.95
4	16	3	point	magnetite	25.06		1.78	2.79							0.14				58.33		0.28	4.80											93.18
4	16	4	point	magnetite	25.00		1.92	3.09											57.62		0.55	5.17											93.35
4	16	5	point	delafossite	18.71			1.69	0.61				0.17	0.20	0.36				31.07			37.69											90.50
4	16	6	point	delafossite	19.61			1.76											33.40			40.15											94.92
4	16	7	point	magnetite	25.54		1.28	3.61	1.72				0.30		0.36				57.60			2.63											93.04
4	16	8	point	magnetite	26.23		1.50	3.38	0.19						0.45				59.72			4.64											96.10
4	16	9	point	glass	37.88		0.60	7.67	25.37				3.60	2.53					4.73			9.68		0.36									92.42
4	16	10	point	glass	40.28		0.74	7.68	26.45				4.12	1.72	0.22				10.11			4.71											96.03
4	16	11	point	delafossite	26.78		0.58	3.39	4.40				0.34	0.16	0.23				30.78			37.99											104.67
4	18	1	area	bulk	34.98		1.42	4.78	19.50	0.27			2.55	2.37	0.36				19.92			5.59	6.59										98.34
4	18	2	point	copper	1.50			0.81											3.11			96.26											101.69
4	18	3	point	copper	1.32			0.51											3.21			97.08											102.12
4	18	4	point	copper	0.97			0.35											2.54			97.37											101.22
4	18	5	point	copper	0.87			0.27											3.68			95.06											99.88
4	18	6	point	copper	1.27			0.49											2.56			94.52											98.85
4	18	7	point	copper	1.51			0.25											2.83			95.70											100.30
4	18	8	point	glass	38.98		1.64	5.35	24.54	0.41			3.04	4.07	0.27				6.92			5.66	5.63										96.51
4	18	9	point	magnetite	26.46		1.18	2.94	2.07				0.53	0.31	0.56				49.38			0.91	11.71										96.05
4	22	1	area	copper	1.47			0.53											3.27			93.56											98.83
4	22	2	area	copper	1.87			0.64											2.80			92.20											97.51
4	22	3	point	glass	33.53		1.42	1.36	18.55	0.19	0.28		2.78	15.38	0.27			0.24	7.37			7.42	3.79	0.50								0.74	93.82
4	22	4	point	magnetite	25.92		1.61	1.71											59.41			1.69	5.59										95.93
4	22	5	point	copper	1.66			0.63			0.28								3.71			90.96											97.24
4	22	6	point	copper	0.95			0.36											3.11			92.92											97.34

DFC	area	#	type	prov. phase	wt%																												
					O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
5	7	1	area	copper	1.32			0.79			0.23								1.28			95.12	0.57	0.37								1.86	101.54
5	7	2	point	copper	1.27			0.79											1.29		0.38	96.95	0.62										101.29
5	7	3	point	lead	6.51			1.51			1.11								1.34			34.82						<				62.78	108.05
5	7	4	point	sulphide	1.35						22.77								6.68			71.51	<										102.31
5	7	5	point	lead	3.25			0.37			16.18								4.74			60.61	<									19.71	104.87
5	7	6	point	sulphide	1.29						21.87			0.18					5.98			70.04	0.44									2.01	101.80
5	8	1	point	sulphide	1.13						21.25								3.92			75.58	<										101.88
5	8	2	point	wustite	22.27		1.39	0.26						0.13					69.10			1.15	6.22										100.52
5	8	3	point	wustite	21.80		1.07	0.59	0.38										67.94			0.49	6.49										98.76
5	8	4	point	wustite	20.98		1.24	0.26	0.14					0.18	0.19				67.67				7.04										97.69
5	8	5	point	wustite	20.78		1.20	0.33							0.13				67.65				7.51										97.60
5	8	6	point	wustite	21.28		1.08	0.41							0.12				67.58				7.29										97.76
5	8	7	point	kirschsteinite	33.67		4.98	1.22	14.84				0.14	16.13	0.33			0.26	24.48			0.38	4.64										101.07
5	8	8	point	mixture	33.34		2.01	6.42	15.41				1.41	11.13					15.96			0.37	3.56								9.47		99.07
5	8	9	point	mixture	32.16			11.01	16.56	0.19	0.31		3.29	1.52					5.03				4.77								21.20		96.05
5	8	10	point	mixture	31.32		1.02	8.29	16.46		0.21		2.35	2.99					14.56			0.43	6.95								14.50		99.08
5	8	11	point	mixture	33.88		0.94	9.96	15.88				1.90	6.18					12.34				2.94								16.78		100.80
5	8	12	point	hole	28.23		0.89	8.72	11.82				1.58	9.01					14.46			0.59	3.96								10.21		89.47
5	8	13	point	hole	34.48	2.22	0.31	15.54	17.78				13.11	3.24					6.52				2.30				0.34				3.25		99.08
5	9	1	point	hercynite	28.34		2.29	10.30	0.18						0.56				52.70				7.20										101.57
5	9	2	point	hercynite n	26.78		1.97	11.13	0.16					0.18	0.73				50.75				8.24										99.93
5	9	3	point	Zn-wustite	21.91		2.12	0.58	0.18										69.81				4.52										99.12
5	9	4	point	copper	1.39			0.62											5.69			95.08											102.79
5	9	5	point	sulphide	2.02			0.37			19.90								8.88			72.66											103.83
5	9	6	point	copper	1.67			1.12											4.13			93.45											100.36
5	9	7	point	Zn-wustite	22.07		1.09	0.27	0.19					0.20					67.01			0.39	7.31										98.54
5	9	8	point	Zn-wustite	23.65		1.09	0.77	0.43					0.57	0.34				65.11				8.19										100.15
5	9	9	point	kirschsteinite	32.01		1.97	3.77	14.92				0.98	12.26					22.26				5.84								4.90		98.91
5	9	10	point	copper	1.30			0.93											4.46		0.31	95.44											102.44
5	9	11	point	sulphide	1.69						22.87								10.16			66.33										2.10	103.14
5	10	1	area	bulk:	10.62			0.46	0.35		2.21	0.25										85.16						0.50			0.46		100.01
5	10	2	point	cuprite	9.78			0.23				0.42										86.69								0.55			97.66
5	10	3	point	barite / anglesite	25.07						13.38											5.35									31.85	35.55	111.20
5	10	4	point	Zn-magnetite	24.76			0.52							0.28				61.76			2.39	12.03										101.74
5	10	5	point	cuprite	9.75																	88.26											98.01
5	10	6	point	glass?	49.12			1.15	27.02	0.22			0.44	0.44	0.19				21.04			2.36	1.44	2.65									106.06
5	10	7	point	magnetite	30.43		1.64	14.13	0.21						1.51				47.47				10.62										106.01
5	10	8	point	olivine	33.11		4.76	1.48	14.79				0.97	6.40					31.30				7.22								0.47		100.50
5	10	9	point	mixed sulphate	20.05						9.93											22.72									23.64	27.15	103.48
5	10	10	point	mixed sulphate	21.51				0.34	0.17	12.13											4.06									40.43	20.29	98.92
5	10	11	point	cuprite	15.82			4.33	1.00										0.13			85.26	<										106.54
5	11	1	point	chalcocite:	0.43						21.08											81.51	<										103.02
5	11	2	point	chalcocite:	0.52						21.02											81.06	<									2.22	104.82
5	11	3	point	cuprite	10.40																	91.46	<										101.86
5	11	4	point	cuprite	10.52				0.25			0.44										88.85	<										100.06
5	11	5	point	chalcocite	0.61						21.07											80.79	<									1.43	103.90
5	11	6	point	mixed sulphate	17.80						11.06											4.70									36.66	22.91	93.12
5	11	7	point	olivine	34.05		2.96	0.27	15.16				0.13	15.56				0.24	28.63				6.66										103.65
5	11	8	point	Zn-wustite	22.10			0.43						0.18					58.72			10.47	8.69										100.58
5	11	9	point	cuprite	14.39			0.34	1.34			1.03		0.33					5.91			75.39		1.03									99.76
5	11	10	point	mixture	32.50		3.29	11.77	7.87				0.20	4.50	0.46				29.86				13.68										104.12

DFC	area	#	type	prov. phase	wt%																												
					O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
5	11	11	point	mixed sulphate	21.25						12.33											6.30									42.97	18.00	100.85
5	11	12	point	Zn-wustite	22.59			0.39	0.29										64.49			0.97	11.47										100.19
5	11	13	point	Zn-Al-magnetite	31.78		1.97	19.61	0.61						0.72				33.93			0.81	15.56										104.98
5	11	14	point	mixed sulphide	2.88			0.63			26.35								1.02			14.82	47.79					0.84				18.65	112.98
5	11	15	area	bulk	31.37		2.07	4.18	10.14		0.15		0.83	5.38	0.24				35.08			2.72	8.85								1.40		102.41
5	12	1	point	magnetite	27.74		1.18	7.83							0.60				55.91				9.34										102.62
5	12	2	point	hercynite	33.55		1.18	22.82	0.38					0.26	0.69				29.89				21.14										109.92
5	12	3	point	wustite	21.74		0.71	0.54	0.18					0.15					67.65				7.76										98.73
5	12	4	point	magnetite?	24.01			0.72	0.18					0.18					62.97				12.73										100.81
5	12	5	point	olivine	33.12		4.62		14.88					13.88				0.22	28.81				6.50										102.02
5	12	6	point	olivine	34.41		4.16		15.10				0.14	14.23					28.91				6.39										103.34
5	12	7	point	copper	2.19			2.05											5.24			94.60	1.89	1.45									107.41
5	12	8	point	mixed	16.34			1.19	1.07		1.32	4.18							26.91			12.45	2.40	6.62								22.31	94.79
5	12	9	point	mixed	30.20			4.11	16.07	0.32			3.80	2.47					12.02				14.44				0.45				20.13		104.00
6	3	1	area	bulk	32.43		0.49	2.89	14.30	0.18			0.91	4.85					25.71			0.95	15.79	<								2.70	101.18
6	3	2	point	willemite	27.30		1.39		12.31										16.63				38.33										95.96
6	3	3	point	willemite	27.92		1.53		12.77										17.38				37.10										96.69
6	3	4	point	glass	34.74			4.07	16.78	0.30	0.18		2.02	10.99					16.48				8.12									4.45	98.14
6	3	5	point	fayalite	29.95		0.70		13.09					2.59					42.86				8.68										97.87
6	3	6	point	fayalite	30.47		1.12		13.45					1.73					43.81				8.79										99.38
6	3	7	point	cuprite	9.41							0.21							2.83			84.73											97.18
6	3	8	point	cuprite)	7.28			0.79	0.87		1.81			0.19					9.39			66.05	2.67									10.69	99.75
6	4	1	area	bulk	31.99		0.67	2.68	14.74				0.86	4.12					24.16			0.36	19.29	<								2.32	101.18
6	4	2	point	willemite	27.44		1.54		12.60										14.03				41.49										97.11
6	4	3	point	magnetite	24.85			3.69	0.21						0.83	0.22	0.26		59.92				7.62										97.61
6	4	4	point	fayalite	29.45		1.10		13.40					1.52				0.22	43.85				9.16										98.69
6	4	5	point	fayalite	28.46		0.80		12.80					2.26					43.17				8.97										96.47
6	4	6	point	glass	33.94			4.59	17.09	0.36			2.26	10.60					15.31				7.92									5.03	97.09
6	4	7	point	willemite	28.10		1.62		13.10										15.71				41.47										10<
6	4	8	point	glass	34.08			4.46	16.55	0.27			1.76	10.74					20.74				6.88									5.85	101.34
6	4	9	point	glass	34.45			4.37	16.63	0.31			2.10	11.15					18.27				5.35									6.28	98.91
6	4	10	point	copper/ sulphide	1.82			0.26			11.00								2.03			88.92											104.03
6	4	11	point	magnetite	26.52			3.70	0.20						0.75	0.21			62.93				7.68										101.99
6	5	1	area	copper	1.80			0.60													1.04	82.11		3.10								14.47	103.12
6	5	2	point	copper)	0.69			0.32											0.23		1.36	94.63	<	4.27									101.50
6	5	3	point	chalcocite	0.46						20.27								0.65			78.85	<									1.32	101.54
6	5	4	point	chalcocite e	1.74						18.06								1.12			79.18										1.98	102.08
6	5	5	point	fayalite	29.94		1.20		13.38					1.75					43.40			1.21	9.41										100.30
6	5	6	point	willemite	28.45		1.68	0.24	13.00										17.22				39.96										100.54
6	5	7	point	magnetite	25.39			4.49							0.49		0.31		60.58				8.65										99.92
6	5	8	point	glass	35.34			4.71	17.62	0.49			2.34	11.90					15.14				7.68									3.45	98.66
6	5	9	point	hercynite	32.62			24.03	0.25						0.58	0.17			25.16				22.73										105.53
6	5	10	point	willemite	24.40		0.97	1.09	10.29						0.19				24.32				32.71										93.96
6	5	11	point	glass	36.94			6.24	18.10	0.52	0.16		3.04	10.99	0.21				13.22			0.59	6.50	<								2.84	99.35
6	5	12	point	willemite	28.35		1.51	0.22	12.94										21.29				34.73										99.04
6	5	13	point	glass	35.85			6.20	17.83	0.46	0.20		2.83	11.17	0.27				13.58				8.50	<								2.79	99.67
6	5	14	point	fayalite	29.07		0.82		13.19					2.08				0.23	44.17				8.59										98.16
6	5	15	point	magnetite	24.83			6.52	0.40					0.28	1.23	0.56	1.00		51.71				10.68										97.20
6	5	16	point	glass	34.41			5.16	17.32	0.30			2.65	10.80	0.20				14.36				8.07									3.04	96.31
6	5	17	point	glass	34.11			4.58	17.05	0.34			2.21	11.12	0.19				15.50				8.75	<								2.90	96.75
6	5	18	point	glass	37.69			5.82	18.31	0.47	0.21		2.62	11.69	0.18				15.21				8.55	<								3.15	103.90

DFC	area	#	type	prov. phase	wt%																												
					O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
6	5	19	point	willemite	29.34		1.60		13.21										19.79				37.99										101.93
6	5	20	point	lead oxide	13.29			4.75														18.78		0.62								85.40	122.84
6	7	1	point	Zn-wustite	22.15		0.37	0.25	0.28										68.09			0.52	8.45										100.11
6	7	2	area	bulk	1.89			0.84											0.50		1.07	81.10		4.21								11.40	101.00
6	7	3	area	bulk	21.97		0.53	1.33	2.48					0.14					44.53		0.30	18.06	9.90									0.79	100.04
6	7	4	point	glass	35.19			4.53	16.80	0.38			1.94	11.81	0.18				17.23				7.46									1.82	97.35
6	7	5	point	glass	30.65			1.37	11.06	0.16				0.41					21.94			3.71	10.76	0.51								10.04	90.60
6	7	6	point	cuprite	9.05				0.18			0.58							2.03			81.86	1.26										94.95
6	7	7	area	copper	2.61			0.85	0.33		0.27								2.78		1.98	87.55		4.20								1.43	101.99
6	7	8	point	copper	0.58														0.48		1.48	92.11		4.88									99.98
6	7	9	point	zinc sulphide	1.22						30.77								2.65			9.35	56.72						0.56			1.51	102.78
6	7	10	point	chalcocite	0.55						20.15								0.46			78.87											100.03
6	7	11	point	copper	0.73						0.23								0.82		1.26	92.53	1.54	5.50						0.40			103.01
6	7	12	point	cuprite	10.07							1.67							2.00			85.05										1.68	100.47
12	17	1	area	cuprite	8.21			0.63			0.21	0.45							0.37			78.47	<					0.43					88.77
12	17	2	area	hydrated oxide?	20.45			1.06	4.01		0.21								0.36			41.34		1.49				0.66					69.58
12	17	3	area	Cu/Ag oxide?	1<			1.61	0.16		0.32	0.33							0.46			41.68						41.77					96.33
12	17	4	area	silver	9.87			0.42	<		2.27	0.37							0.41			67.80	<					13.39				<	94.51
12	17	5	point	ialteration	5.58			0.17	0.14		0.33	1.35							0.44			77.23	<										85.24
12	17	6	point	cuprite	7.89			0.24			<	0.14							0.44			81.41	<									<	90.13
12	17	7	point	cuprite	9.22						0.23	0.21							0.44			82.85	<									<	92.94
12	17	8	point	cuprite	8.75			0.24	<		0.22								0.53			81.96	<									<	91.70
12	17	9	point	hole	7.29			2.59	0.86		0.67	1.97		0.14					0.39			69.75						0.41					84.07
12	18	1	area	glass	37.44	1.20	1.10	11.08	24.90	0.36			2.22	0.30	0.59				6.34			2.26											87.79
12	18	2	area	glass	36.34		1.88	9.14	21.88	0.35			1.37	2.67	0.46			0.23	11.05			4.54	3.24									1.63	94.79
12	18	3	area	glass	39.97	0.92	1.39	10.62	24.25	0.25			1.97	0.93	0.55			0.23	9.59			3.74	0.62										95.03
12	19	1	point	copper	1.00			0.50											1.73			90.47	<										93.69
12	19	2	point	mixture	14.11		1.05	5.02	9.48		0.49		0.45	1.12	0.16				5.19			64.76	1.03									0.72	103.58
12	19	3	point	mixture	11.87		1.03	3.97	7.64		0.21		0.30	0.80					4.04			75.84		<									105.71
12	19	4	point	mixture	23.44		1.45	6.57	14.87	0.25	0.14		0.71	1.91	0.31				7.33			42.27	2.20									0.93	102.39
12	19	5	point	mixture	19.23		1.32	5.92	11.84		0.32		0.50	1.33	0.22				5.05			61.88	1.30									0.75	109.65
12	19	6	point	mixture	17.77		1.03	4.57	9.64		0.27		0.46	1.18	0.22				5.36			61.36	1.47									0.73	104.06
12	19	7	point	mixture	17.14		1.21	4.94	9.66		0.30		0.32	1.09	0.19				4.70			68.23	1.09									0.79	109.67
12	19	8	point	mixture	20.42		1.33	5.76	11.28				0.39	1.13	0.22				5.41			65.73	1.31									0.80	113.77
12	19	9	point	mixture	34.42		1.85	8.08	20.71	0.29			0.98	3.12	0.49			0.28	11.89			3.86	3.53	<								1.68	91.18
13	2	1	area	copper	5.24			0.48														93.71		0.65									100.08
13	2	2	point	cuprite	9.21			0.21				0.75										88.24											98.42
13	2	3	point	cuprite	5.99			0.78			0.19	0.33										90.70		0.67									98.66
13	2	4	point	copper	1.81			0.39													<	98.22		0.59									101.02
13	2	5	point	copper	1.22			0.64													0.30	101.12		0.57									103.85
13	3	1	area	bulk	46.24	0.83	0.73	8.02	32.29	0.23	<		1.81	0.19	0.46				4.02			0.32											95.15
13	4	1	area	cuprite	10.18			0.32														83.44	<										93.93
13	4	2	area	hydrated oxide?	22.56			0.93	3.48	0.51	0.24	0.16		0.17					0.26			39.78		2.27									70.38
13	4	3	point	glass	42.65	0.86	1.66	10.79	24.50	0.21			2.52	4.06	0.55			0.25	7.34			4.47	0.72										100.58
14	2	1	point	qtz/fspar	65.01		0.29	4.31	44.35		0.12		0.83						0.68			3.37										<	118.95
14	2	2	point	qtz/fspar	14.14		0.31	7.25	16.72	0.30		0.13	2.16	0.40	0.72				1.34			13.64											57.10
14	2	3	point	hydrated oxide?	23.27				0.42		6.19	1.72							0.80			61.89	<									1.00	95.28

DFC	area	#	type	prov. phase	wt% O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
14	2	4	point	hole	1.86			1.41	0.17		0.15	0.07		0.68					2.17			9.00						0.92					16.42
14	2	5	point	goethite?	33.34				0.42					0.12					58.69			1.50	0.44	0.37									94.87
14	2	6	point	goethite?	31.59			0.35	0.45										55.14			2.26											89.79
14	2	7	point	hydrated oxide?	27.14			0.22											1.16			50.16	<										78.68
14	2	8	point	hydrated oxide??	21.82				0.16		6.33											51.47	<										79.77
14	2	9	point	hole?	11.77		0.32	7.07	1.33	1.61	0.42	0.66		2.71					8.04			2.64											36.55
14	2	10	point	hole?	13.60		0.27	4.49	0.24	0.88	0.41	0.12		2.29					0.17			10.74											33.19
14	2	11	point	hydrated oxide?	32.08			0.51	0.40										0.96			60.79	<										94.74
14	2	12	area	hydrated oxide?	24.75			0.77			1.00											43.98	<										70.51
14	2	13	area	bulk	26.84			1.22	0.80		0.26	0.11							18.85			28.98	<										77.07
14	2	14	area	bulk	21.53			1.23	1.50		0.18	0.24							34.14			3.11		0.40									62.33
14	2	15	area		33.44		0.39	5.77	15.60	0.22	1.93		1.07	0.23	0.17				1.06			25.83											85.72
14	2	16	point		30.28			2.02	3.66	0.18		0.20	0.13	0.17					43.06			6.54		0.57									86.79
14	2	17	point	silver	15.15		0.39	1.60	0.27		9.13								1.63			3.56						83.39					115.12
14	2	18	point		34.17			0.24	0.37	0.18	0.25	0.13							56.82			2.39		0.70									95.25
14	2	19	point		29.51				0.38		0.19								50.32			2.77		0.60									83.77
14	2	20	point	Cu oxide?	26.67														1.33			49.67	<										77.66
14	2	21	point	Cu oxide?	20.38				0.14		6.27											53.29	<										80.08
14	2	22	point	Cu oxide?	24.84														0.23			49.81	<										74.88
14	3	1	point	Cu oxide?	23.46			0.22														43.19	<										66.87
14	3	2	point	iron oxides	11.15			0.78	1.14	0.27		0.13		0.28					17.38			4.39											35.51
14	4	1	area	bulk	47.40	1.02		6.55	19.58	0.49	0.23	0.15	0.71	0.22	0.25				34.04			4.19		1.56									116.40
14	4	2	area	bulk	40.31	1.18	0.66	9.03	23.75	0.47		0.16	1.23	0.39	0.46				5.00			8.16											90.79
14	4	3	area	bulk	10.56			1.98	2.19	0.32	0.11	0.24		0.42					7.22			4.63											27.68
14	4	4	point	quartz	42.97				38.00													0.35											81.32
14	4	5	point	quartz	50.61				45.42										0.28														96.32
14	4	6	point	glass?	42.81		0.82	8.29	28.21	0.56		0.29	0.76	0.23					6.82			7.87		0.28									96.93
16	7	1	point	malachite	32.19			0.54														48.79	5.32										86.84
16	7	2	point	malachite	28.70														0.68			47.46	5.76										82.59
16	7	3	point	malachite	29.30														0.22			46.53	7.33										83.38
16	7	4	point	malachite	28.07														0.28			46.76	6.70										81.82
16	8	1	area	anglesite	16.32			0.72	0.46		9.01																					57.40	83.90
16	8	2	area	malachite	29.42			1.17	0.53		0.90								0.28			39.97	5.29					5.64					83.20
16	8	3	area	malachite	22.85			0.93	0.24										0.25			39.48	5.01										68.76
16	8	4	point	sediment	26.30		0.92	9.73	23.45	0.24	0.14	0.15	3.16						1.33			1.84	0.34										67.60
16	8	5	point		4.88							0.96																					5.83
16	8	6	point	quartz	29.01			1.21	29.86										1.16			0.76											62.00
16	8	7	point		1.00			0.70	0.07													0.44											2.21
16	10	1	point	silver	20.66		0.32	0.34			5.96											10.27	1.31					73.85					112.71
16	10	2	point	sediment	34.63		1.26	12.44	26.36	0.27		0.20	3.54						1.36			1.07	0.43									0.58	82.15
16	10	3	point	malachite	23.55			0.35	0.20												0.33	45.42	6.17										76.03
16	10	4	point	malachite	26.36			0.34											0.49			46.12	6.07										79.37
16	11	1	area	bulkt	25.94			0.57	1.04	0.91	3.64	<							23.74			3.11	0.58	0.70				24.76				7.57	92.56
16	11	2	area	bulk	30.93				3.21	1.01									38.66			6.64	0.69	0.82								10.09	92.05
16	11	3	area	bulk	19.72			0.66	1.65	0.33		0.16		0.12					29.08			5.91	1.69	0.48								1.94	61.75
16	11	4	area	bulk	31.21				2.20	0.26									45.58			3.84	4.21	0.69								1.37	89.36
16	11	5	point	silver	35.26			0.27	1.62	0.54	6.69						0.21		24.32			2.88		<				35.58				6.02	113.39
16	11	6	area	bulk	28.48			0.81	2.45	0.56		0.13		0.15					36.97			6.21	1.83	0.62				0.63				4.97	83.80

DFC	area	#	type	prov. phase	wt%																												
					O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Zr	Mo	Ag	Cd	Sb	Ba	Pb	total
16	12	1	area	chalcopyrite							37.74								33.30			35.85	<									1.56	108.45
18	7	1	point	mimetite	11.72							2.33		0.65										14.99								69.72	99.41
18	7	2	point	mimetite	15.44							1.79		0.70								0.44		11.72	3.60							60.13	93.82
18	7	3	area	mimetite	13.63							1.99		0.66										13.68	1.06							64.75	95.77
18	7	4	area	azurite	28.50			0.31														54.73	<										83.54
18	8	1	area	bulk	29.41			2.03	2.29		0.72		0.16						0.43			50.13						0.88					86.05
18	8	2	area	silver bulk	32.35			0.77			1.56											45.66	<					9.32					89.66
18	8	3	point	azurite	27.39			0.19	<													53.96	<										81.54
18	9	1	point	rosasite	29.08		0.51	0.80														33.45	27.94										91.77
18	9	2	point	rosasite	25.49			5.50	0.19			0.15										28.38	20.39										80.11
18	9	3	point	rosasite	17.90														0.18			20.65	19.89										58.62
18	9	4	point	rosasite	25.26	1.34		0.30														31.35	21.66										79.92
18	9	5	point	rosasite	22.58							0.13										25.02	23.76										71.49
18	9	6	area	rosasite	22.68	1.30	0.35	0.58				0.14										25.89	20.97										71.91
18	9	7	point	rosasite	15.14			0.33				0.19										20.59	17.46										53.71
18	10	1	point	siderite?	3.37							1.15							0.14			0.47											5.12
18	10	2	point	siderite?	36.44			2.08	1.94	1.55				0.39					41.22			8.92	1.96	3.62								2.29	100.41
18	10	3	point	malachite	25.59			0.64													0.40	46.43	9.15	0.61									82.83
18	10	4	point	malachite	18.12			1.32				0.16							0.76		0.39	39.96	5.73	0.78									67.24
18	10	5	point	zircon	25.32				12.52													1.81	0.47			41.89							82.02
18	10	6	area	bulk	26.93		0.27	2.50	13.65			0.15	0.16						0.57		0.29	24.61	4.12										73.24
18	10	7	area	quartz+siderite	14.43			1.26	4.05	0.44		0.49		0.14					12.56			2.60	0.71	0.89								0.66	38.23
18	10	8	area	malachite	24.43			1.17													0.37	43.05	7.80	0.56									77.39
18	11	1	area	malachite	24.13			0.54	0.23										0.27		0.34	40.11	6.31	0.59									72.53
18	11	2	area	malachite	28.24			0.90			0.92								0.30			38.66	6.16	0.49				5.34					81.02
18	11	3	point	quartz	45.21				44.17		<											0.96											90.34
18	11	4	point	siderite?	22.99			1.24	1.93	0.87				0.26					32.66			6.27	1.91	1.33								1.12	70.58
18	11	5	point	malachite	22.88							0.13									0.43	44.85	7.73	0.86									76.88
18	11	6	point	malachite	24.80		0.26	3.36	3.00	0.21		0.19	0.52		0.29				1.31			35.33	4.80	0.90									74.96
18	11	7	point	silver	27.75		0.32	0.46			8.23											15.66	2.22					86.88					141.51
18	11	8	point	quartz	48.80				47.26													0.64											96.70
18	12	1	point	silver	10.70		0.32				6.74	0.25										2.83	0.68					63.76					85.28
18	12	2	area	bulk	17.31			3.28	2.22	0.22		0.30	0.12					0.39	1.61			20.02	5.16	0.52				0.58					51.71
18	12	3	point	Fe oxides	10.79			1.64	2.99	0.57		0.42		0.21				4.04	2.72	1.63		5.51	3.59	<								1.05	35.15
18	12	4	point	Fe oxides	14.92			2.18	3.41	1.41		0.23		0.49				6.48	9.93	1.44		7.66	4.33	0.82								5.29	58.60
18	12	5	point	Fe oxides	10.89			1.37	2.55	0.61		0.43		0.22				2.69	8.28	0.93		5.18	2.88	0.95								1.08	38.07
18	12	6	point	quartz	41.62				39.62													0.93											82.17
18	12	7	point	malachite	24.28			0.40											0.57		0.38	35.36	11.69	0.76									73.44
18	12	8	area	malachite	21.73			0.90											0.40			33.65	8.77										65.45
18	12	9	area	malachite	13.91			1.35	1.67			0.37	0.21						0.83			18.37	4.67	0.40									41.79
18	12	10	point	malachite	16.92			0.68		0.15		0.13							0.65			34.79	8.30										61.62
18	12	11	point	malachite	21.79			0.36											0.19		0.51	36.63	12.32	0.62									72.44

Table 8: EDS bulk microanalyses of areas of copper. Values in elemental wt%.

sample	Area	#	Fe	Ni	Zn	As	Ag	Sb	Pb	Cu
DFC1	area 3	1	<	<	<	0.75	<	<	<	99.25
DFC1	area 6	2	<	<	<	1.12	<	<	<	98.88
DFC1	area 4	1	<	<	0.56	0.77	<	<	<	98.67
DFC1	area 7	1	<	<	<	0.91	0.44	<	<	98.64
DFC2	area 4	1	0.39	0.53	<	1.32	0.37	<	2.23	95.16
DFC3	area 4	1	1.25	0.36	<	0.77	0.31	<	2.14	95.17
DFC3	area 5	1	1.60	0.45	<	0.77	0.26	<	2.06	94.87
DFC3	area 6	1	0.55	0.26	<	0.96	<	<	3.09	95.14
DFC4	area 2	1	0.68	<	0.90	<	<	<	<	98.42
DFC4	area 2	3	2.60	<	0.88	0.53	<	<	<	95.99
DFC4	area 2	4	2.92	<	0.65	<	0.38	<	<	96.04
DFC4	area 22	1	3.38	<	<	<	<	<	<	96.62
DFC4	area 22	2	2.95	<	<	<	<	<	<	97.05
DFC5	area 7	1	1.29	<	0.58	0.37	<	<	1.87	95.89
DFC6	area 5	1	<	1.04	<	3.08	<	<	14.37	81.52
DFC6	area 7	7	2.84	2.02	<	4.29	<	<	1.46	89.40
DFC6	area 7	2	0.51	1.09	<	4.28	<	<	11.60	82.52

Table 9: EDS microanalyses of points within copper. Values in elemental wt%.

sample	area	#	Fe	Ni	Zn	As	Ag	Sb	Pb	Cu
DFC1	area 3	2	<	<	<	0.87	<	<	<	99.13
DFC1	area 3	3	<	0.31	<	<	<	<	<	99.69
DFC1	area 3	5	<	<	<	2.48	0.80	0.38	<	96.34
DFC1	area 5	1	<	<	<	<	<	<	<	100.00
DFC1	area 6	1	<	<	<	0.45	<	<	<	99.55
DFC3	area 6	4	0.54	0.38	<	<	<	<	<	99.08
DFC4	area 18	2	3.13	<	<	<	<	<	<	96.87
DFC4	area 18	3	3.20	<	<	<	<	<	<	96.80
DFC4	area 18	4	2.54	<	<	<	<	<	<	97.46
DFC4	area 18	5	3.72	<	<	<	<	<	<	96.28
DFC4	area 18	6	2.64	<	<	<	<	<	<	97.36
DFC4	area 18	7	2.87	<	<	<	<	<	<	97.13
DFC4	area 2	5	2.70	<	0.94	<	<	<	<	96.36
DFC4	area 2	6	2.07	0.35	1.15	<	<	<	<	96.44
DFC4	area 2	7	2.95	<	0.76	<	<	<	<	96.28
DFC4	area 2	8	2.52	<	0.96	<	<	<	<	96.51
DFC4	area 2	9	4.69	<	1.06	<	0.41	<	<	93.85
DFC4	area 2	10	4.56	<	1.02	<	<	<	<	94.42
DFC4	area 2	13	3.68	<	0.41	<	<	<	<	95.91
DFC4	area 22	5	3.92	<	<	<	<	<	<	96.08
DFC4	area 22	6	3.23	<	<	<	<	<	<	96.77
DFC4	area 4	2	2.20	<	<	1.14	<	<	<	96.66
DFC4	area 4	3	2.27	<	<	0.94	<	<	<	96.79
DFC4	area 4	4	2.21	<	<	<	<	<	<	97.79
DFC4	area 4	5	3.10	<	<	<	<	<	<	96.90
DFC4	area 4	6	3.64	<	<	<	<	<	<	96.36
DFC4	area 4	7	4.20	<	<	<	<	<	<	95.80
DFC5	area 12	7	5.08	<	1.83	1.40	<	<	<	91.68
DFC5	area 7	2	1.30	0.38	0.63	<	<	<	<	97.69
DFC5	area 9	4	5.65	<	<	<	<	<	<	94.35
DFC5	area 9	6	4.23	<	<	<	<	<	<	95.77
DFC5	area 9	10	4.45	0.30	<	<	<	<	<	95.25
DFC6	area 5	2	0.23	1.35	<	4.25	<	<	<	94.17
DFC6	area 7	8	0.49	1.49	<	4.93	<	<	<	93.08
DFC6	area 7	11	0.80	1.23	1.51	5.39	<	0.39	<	90.67
DFC12	area 19	1	1.88	<	<	<	<	<	<	98.12
DFC13	area 2	4	<	<	<	0.60	<	<	<	99.40
DFC13	area 2	5	<	0.30	<	0.56	<	<	<	99.15
DFC13	area 2	1	<	<	<	0.69	<	<	<	99.31
DFC13	area 2	2	<	<	<	<	<	<	<	100.00
DFC13	area 2	3	<	<	<	0.73	<	<	<	99.27

Table 10: Comparison of copper composition with published microanalyses of impurities in raw copper from the North Welsh Iron Age, and interpreted to be from the Llanymynech area. Data adapted from Northover (1991, Table 2 - data for cobalt, gold and bismuth omitted because they were at levels below detection for the EDS system used in the current study). < = below detection. Four Crosses data are the mean and range of the data in Table 8.

sample	#	Fe	Ni	Zn	As	Ag	Sb	Pb
LBD1: Llwyn Bryn-dinas	1	0.80	0.09	3.76	0.40	0.16	0.14	0.23
	2	0.79	0.11	3.37	0.38	0.11	0.07	0.06
L1: Llanymynech hillfort	1	0.04	0.11	1.02	<	0.42	0.06	0.25
	2	0.05	0.08	1.41	0.88	0.97	0.09	1.04
	3	0.05	0.06	1.03	0.11	0.22	tr	1.00
	4	<	0.07	0.11	0.64	0.43	0.03	0.41
Four Crosses – this study								
Mean value		1.23	0.34	0.21	1.17	0.10	<	2.28
Maximum value		3.38	2.02	0.90	4.29	0.44	<	14.37

Figure 1

Zn v Cu
20.00
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00 5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00
DFC4 - 1
DFC4 - 2
DFC4 - 3
DFC14
DFC16 - 1
DFC16 - 2
DFC18 - 1
DFC18 - 2
DFC18 - 3
DFC18 - 4
Zn v Cu
goethite? - botryoidal
goethite? - between botryoids
goethite? - reticulated
siderite
late weathering products
malachite - botryoidal
malachite pseudomorphs
malachite - prisms radiating
rosasite - botryoidal
azurite
part reacted ore
As v Cu
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
As v Cu
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Fe v Cu
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Fe v Cu

Figure 2

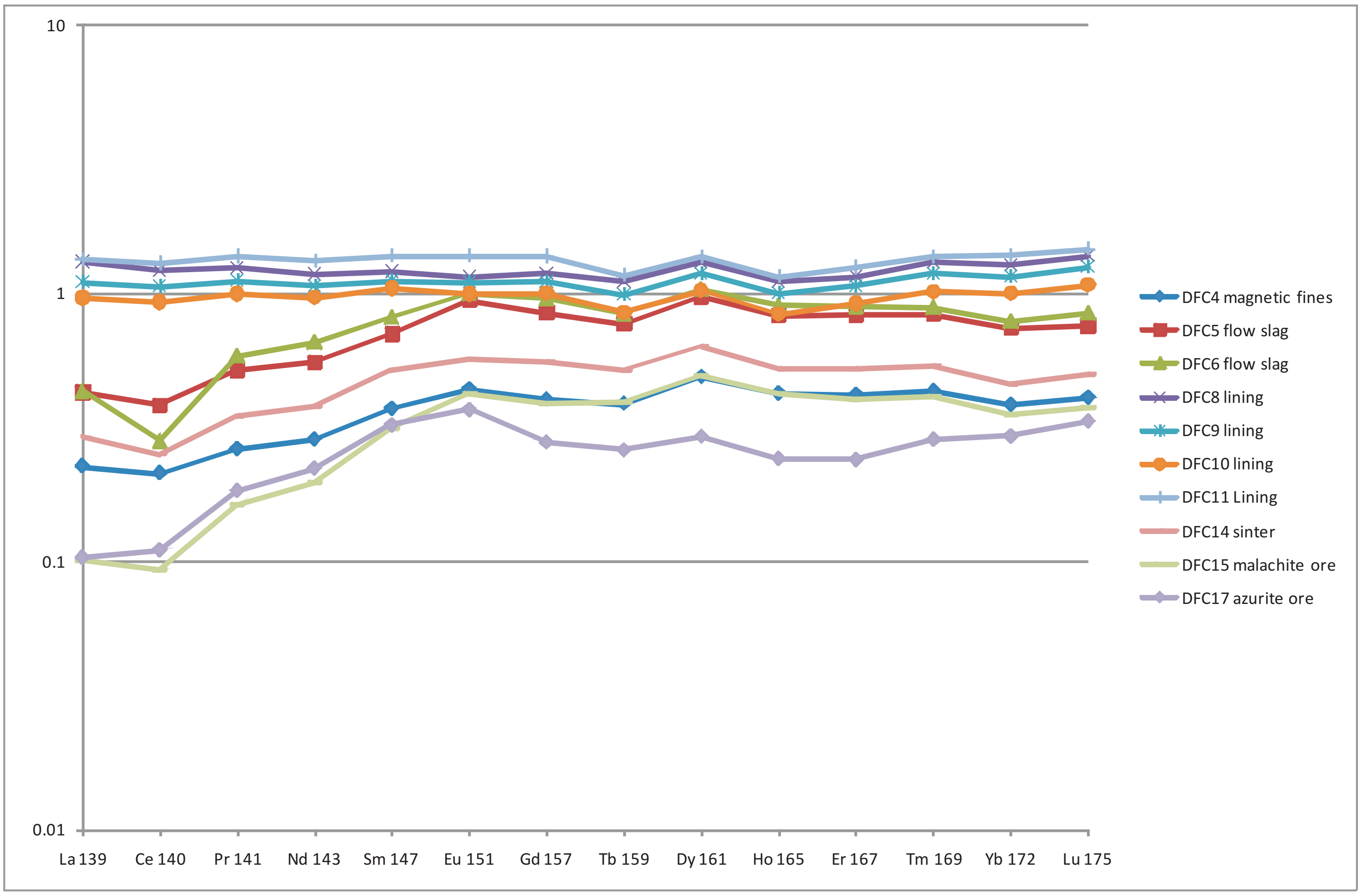

10
1
0.1
0.01
La 139
Ce 140
Pr 141
Nd 143
Sm 147
Eu 151
Gd 157
Tb 159
Dy 161
Ho 165
Er 167
Tm 169
Yb 172
Lu 175
DFC4 magnetic fines
DFC5 flow slag
DFC6 flow slag
DFC8 lining
DFC9 lining
DFC10 lining
DFC11 Lining
DFC14 sinter
DFC15 malachite ore
DFC17 azurite ore

Plate 1

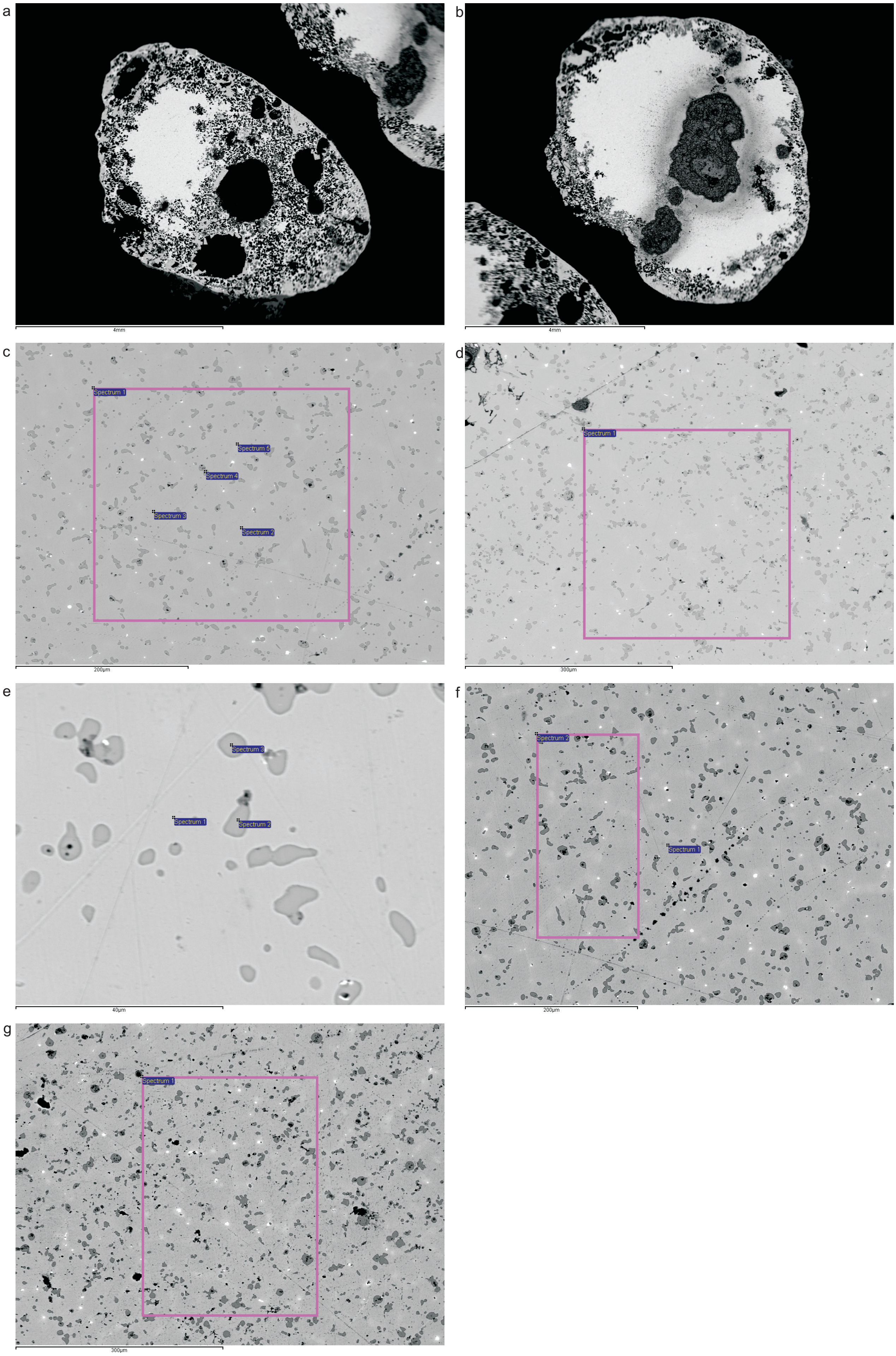

a
4mm
b
4mm
c
Spectrum 1
Spectrum 5
Spectrum 4
Spectrum 3
Spectrum 2
200µm
d
Spectrum 1
300µm
e
Spectrum 3
Spectrum 1
Spectrum 2
40µm
f
Spectrum 2
Spectrum 1
200µm
g
Spectrum 1
300µm

Plate 2

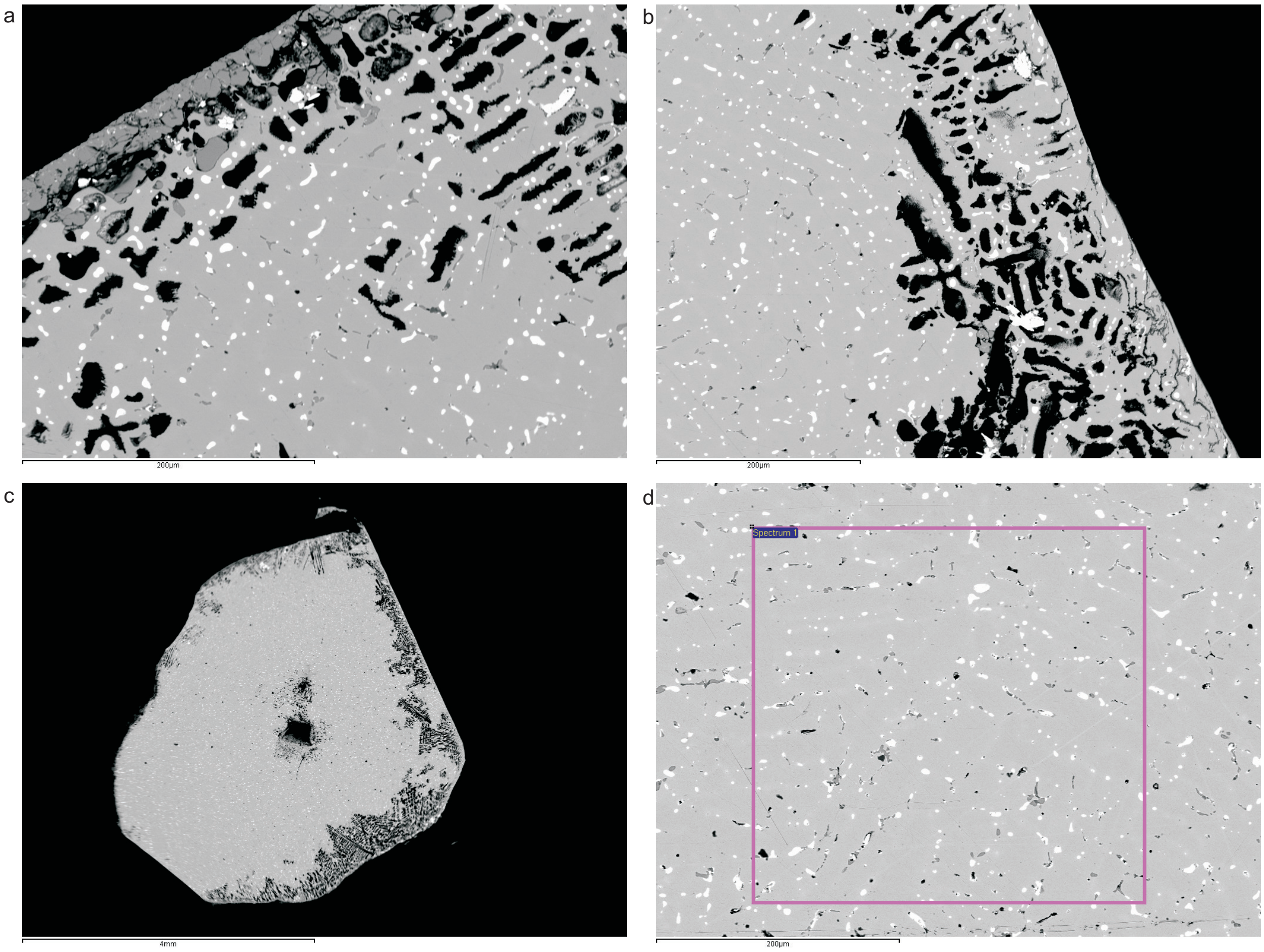
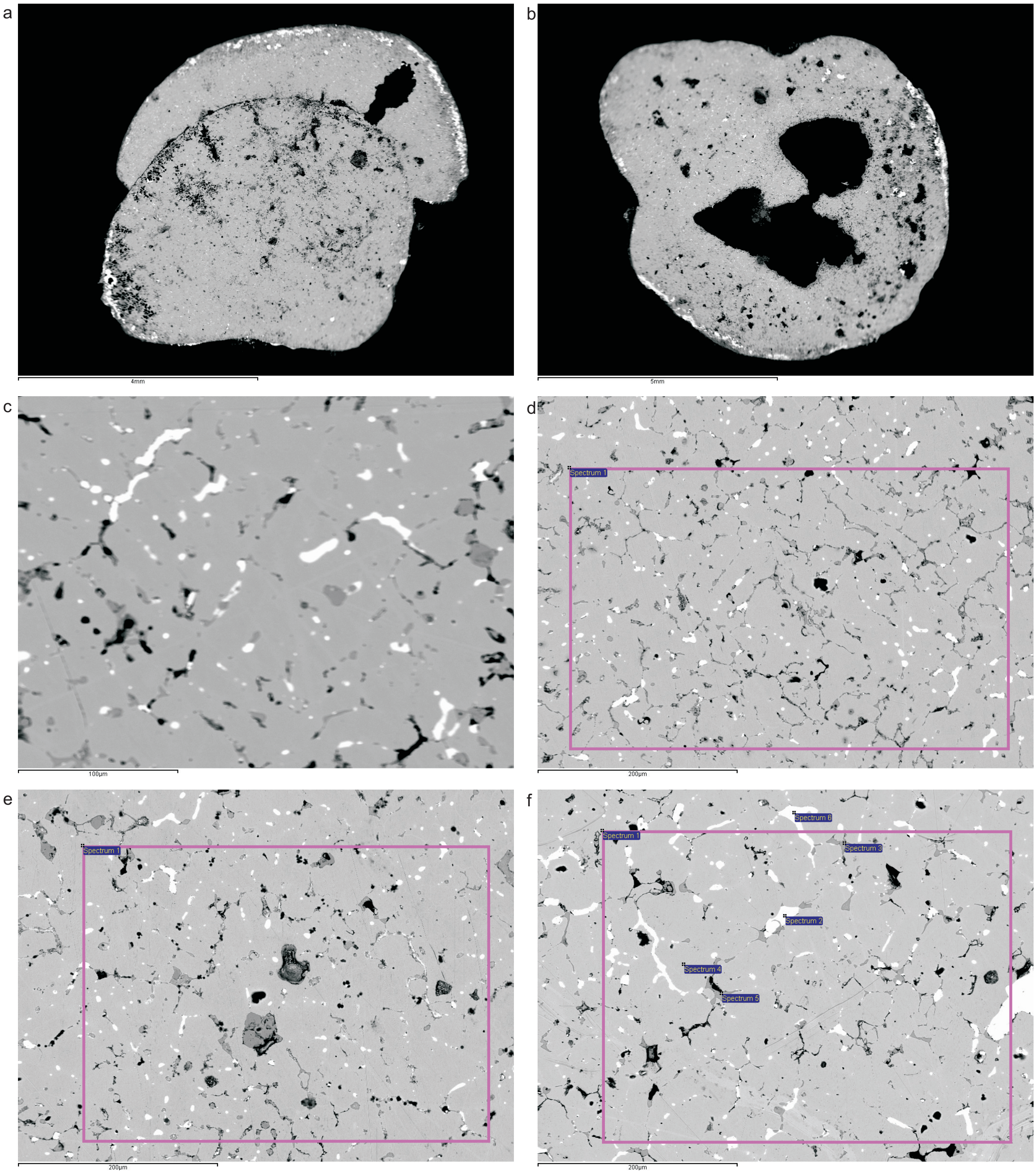


Plate 3



a
b
c
d
e
f
4mm
5mm
100µm
200µm
Spectrum 1
Spectrum 1
200µm
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
200µm

Plate 4

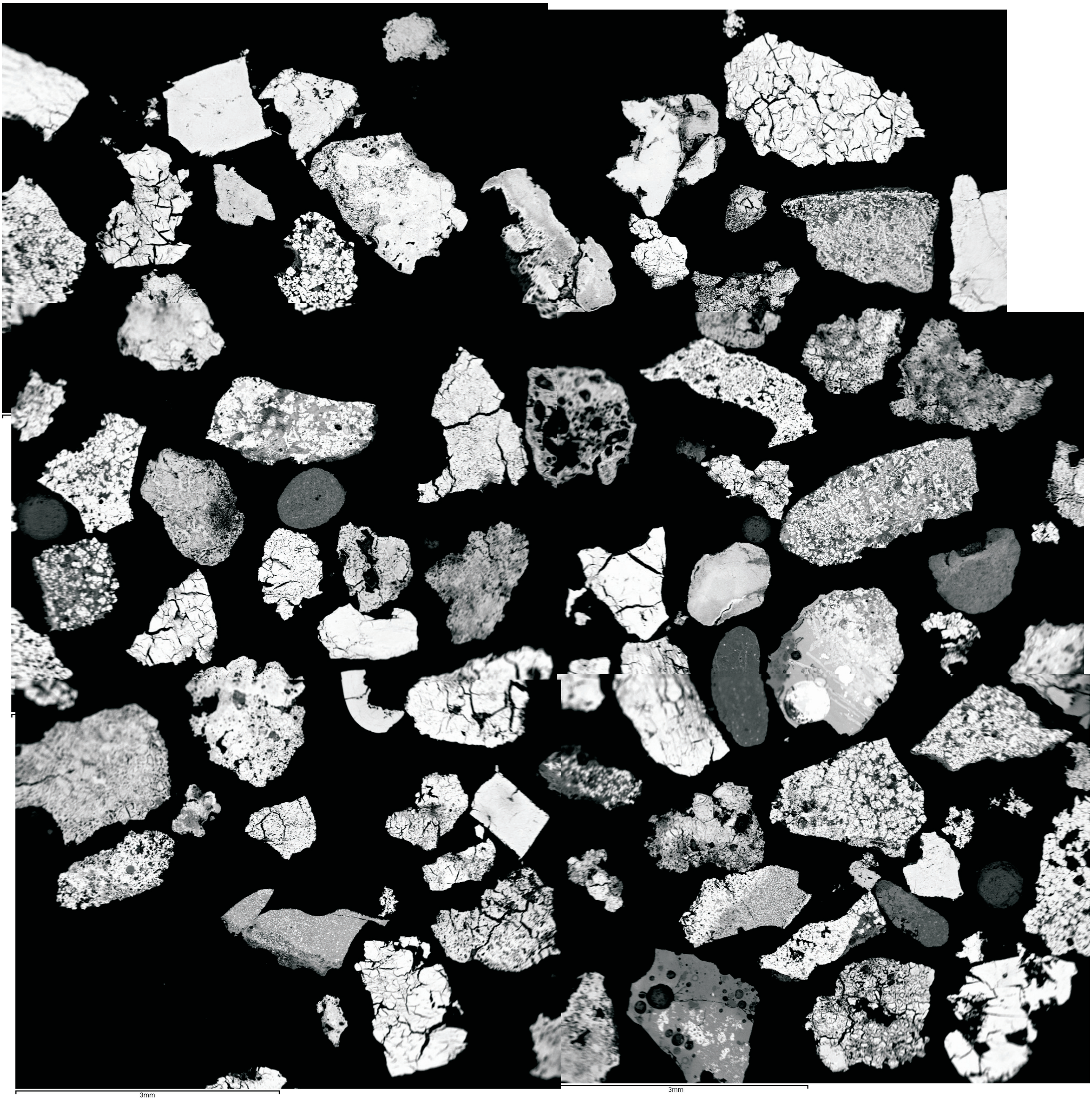
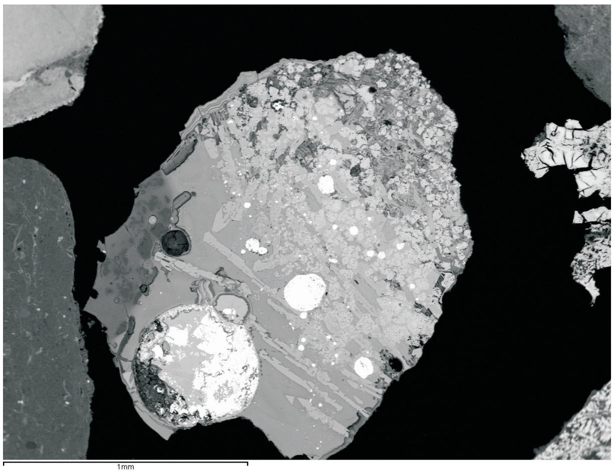
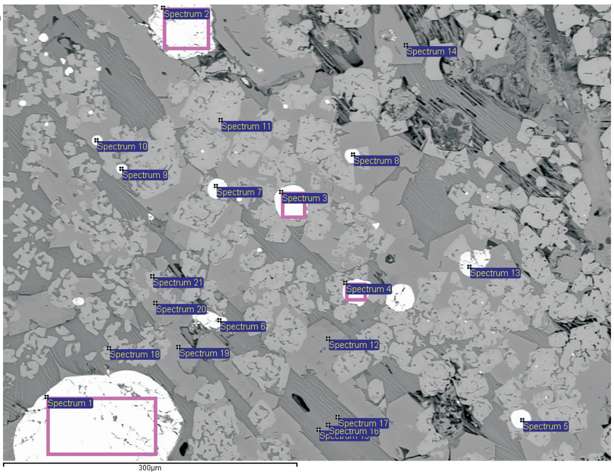


Plate 5

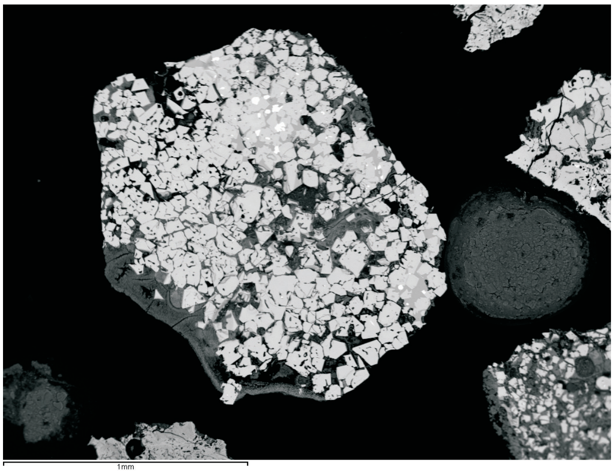
a



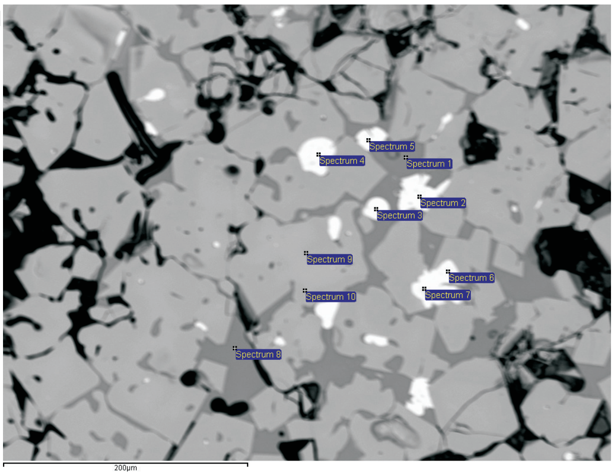
b



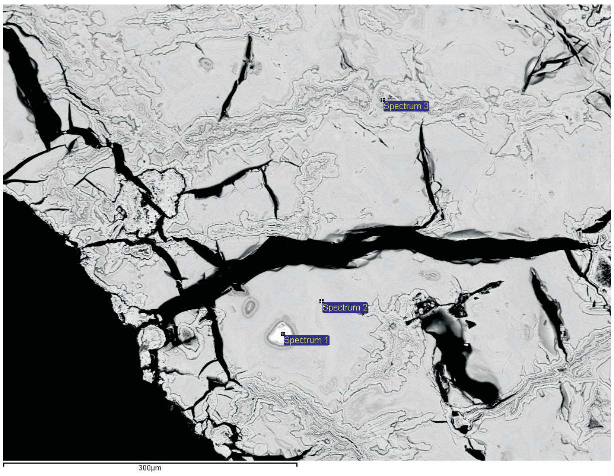
c



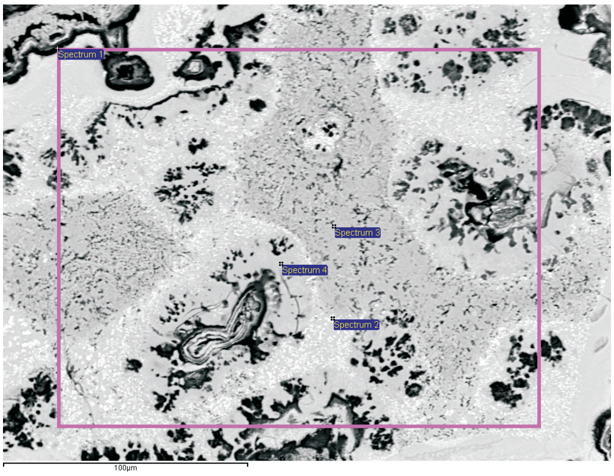
d



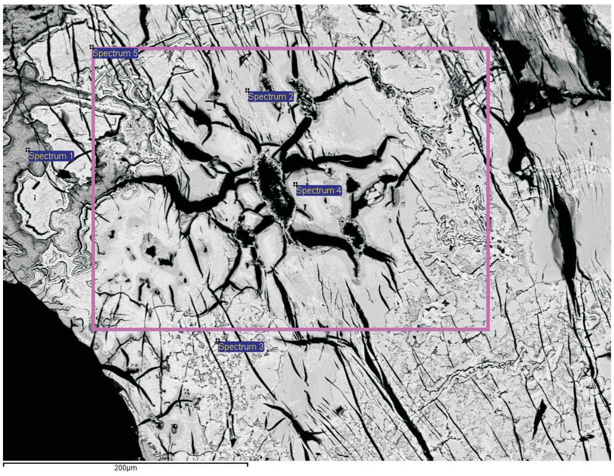
e



f



g



h

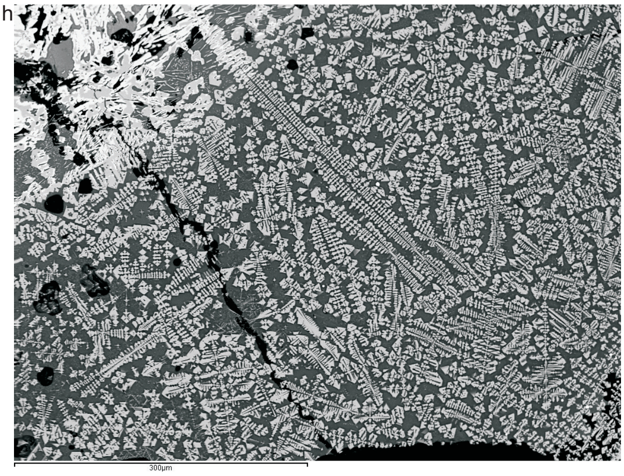


Plate 6

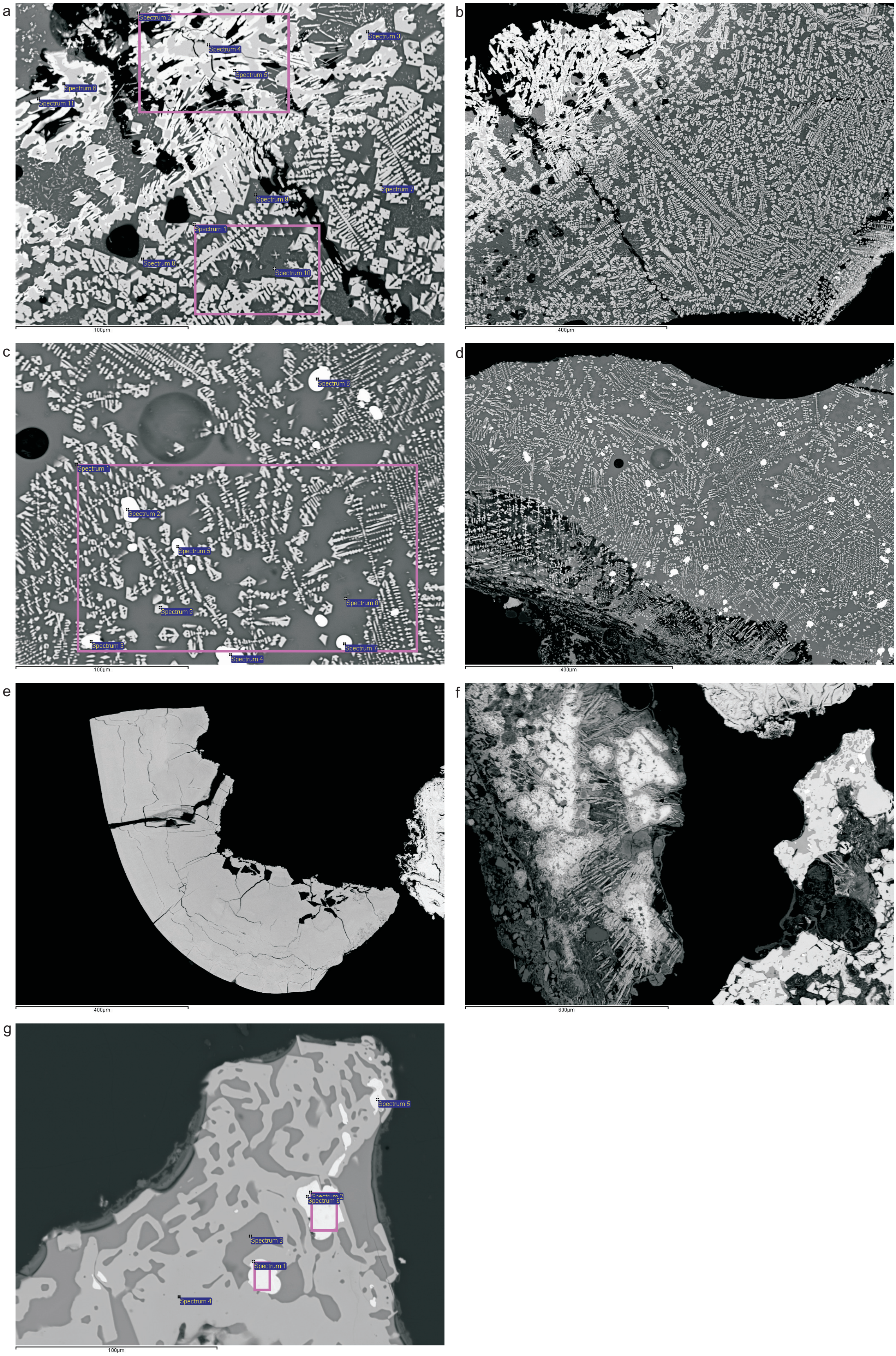

a
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
Spectrum 10
Spectrum 11
100µm
b
400µm
c
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
100µm
d
400µm
e
400µm
f
600µm
g
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
100µm

Plate 7

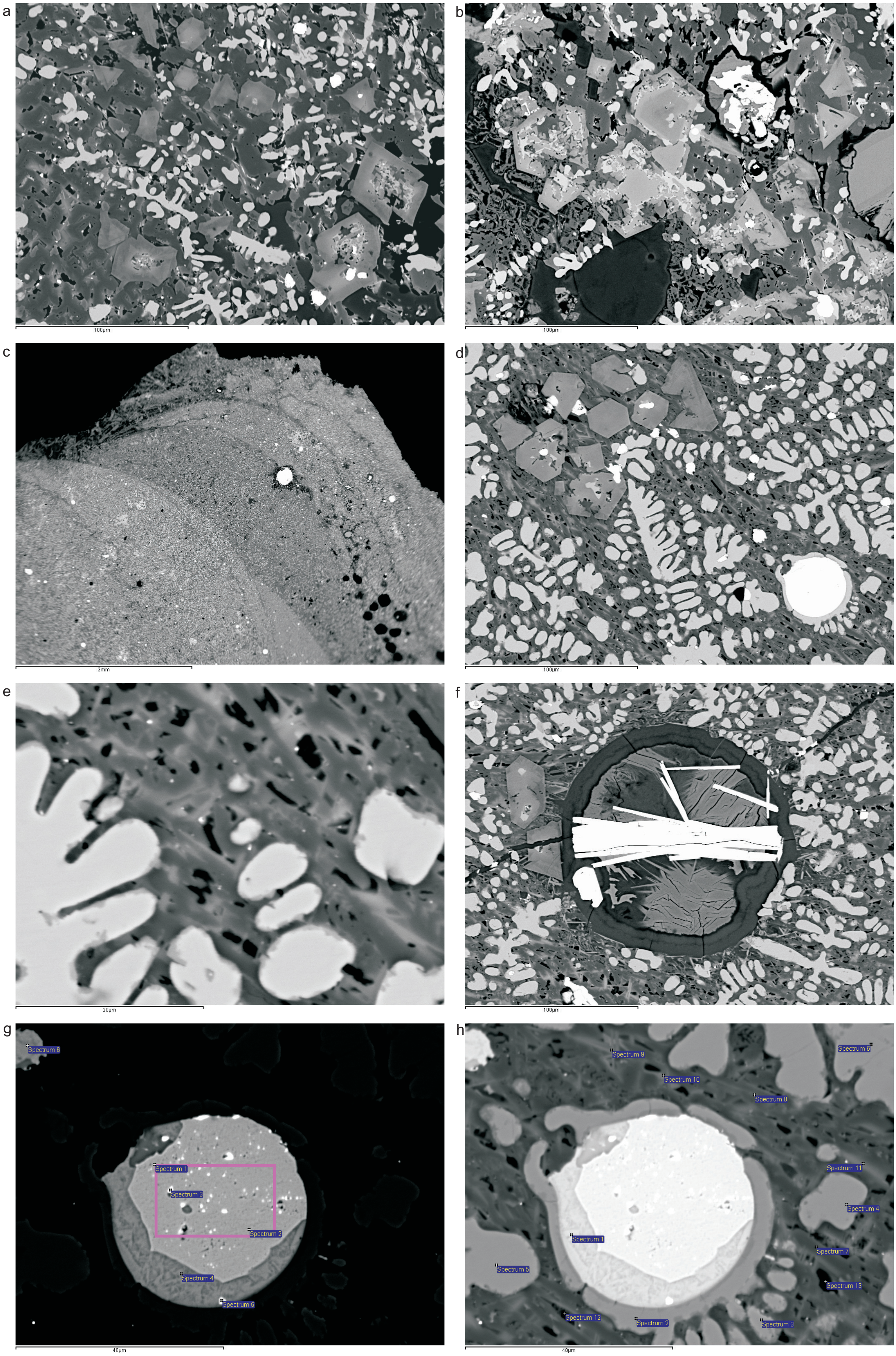

a
100µm
b
100µm
c
3mm
d
100µm
e
20µm
f
100µm
g
Spectrum 6
Spectrum 1
Spectrum 3
Spectrum 2
Spectrum 4
Spectrum 5
40µm
h
Spectrum 9
Spectrum 6
Spectrum 10
Spectrum 8
Spectrum 11
Spectrum 4
Spectrum 1
Spectrum 7
Spectrum 5
Spectrum 13
Spectrum 12
Spectrum 2
Spectrum 3
40µm

Plate 8

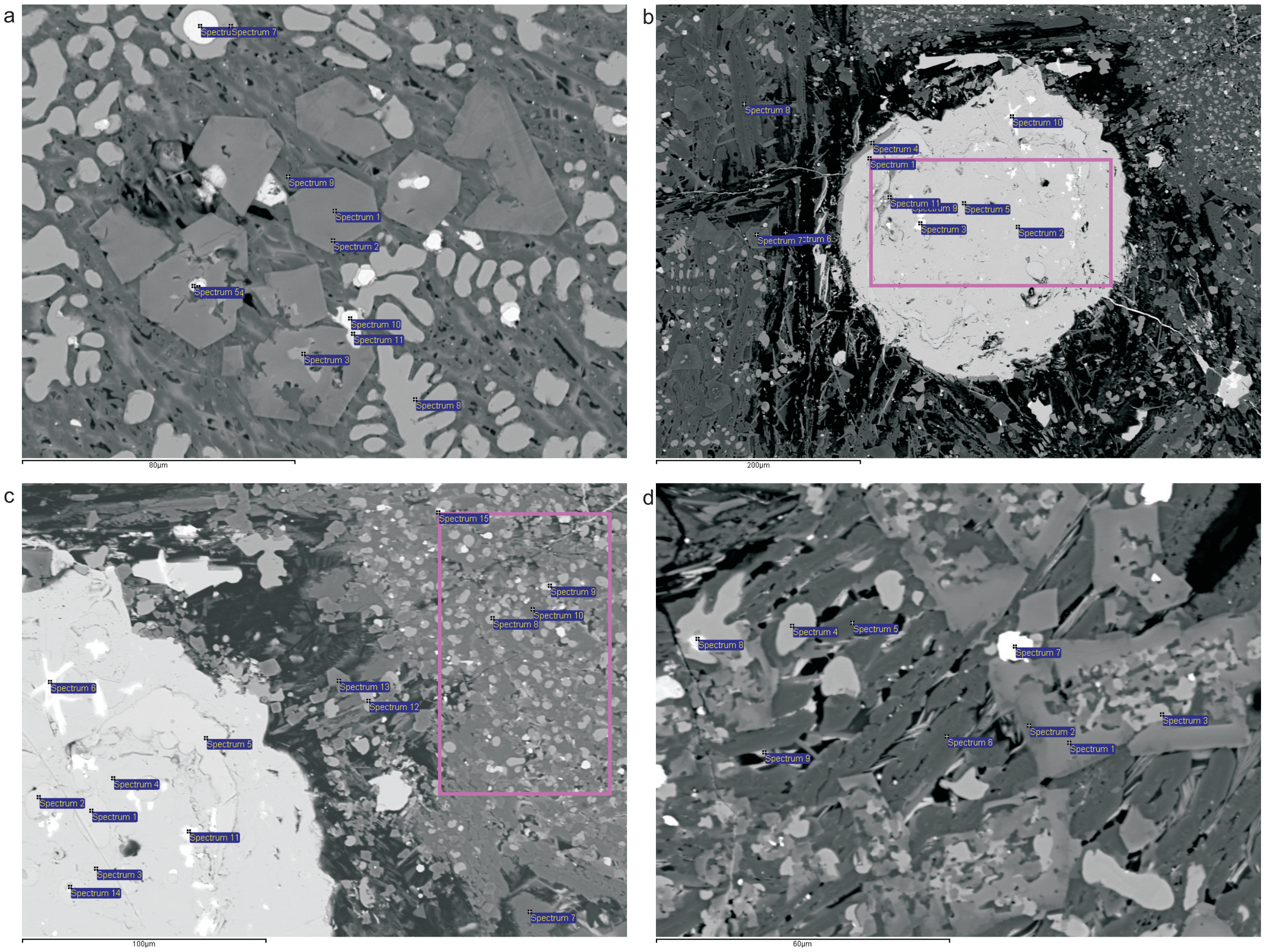
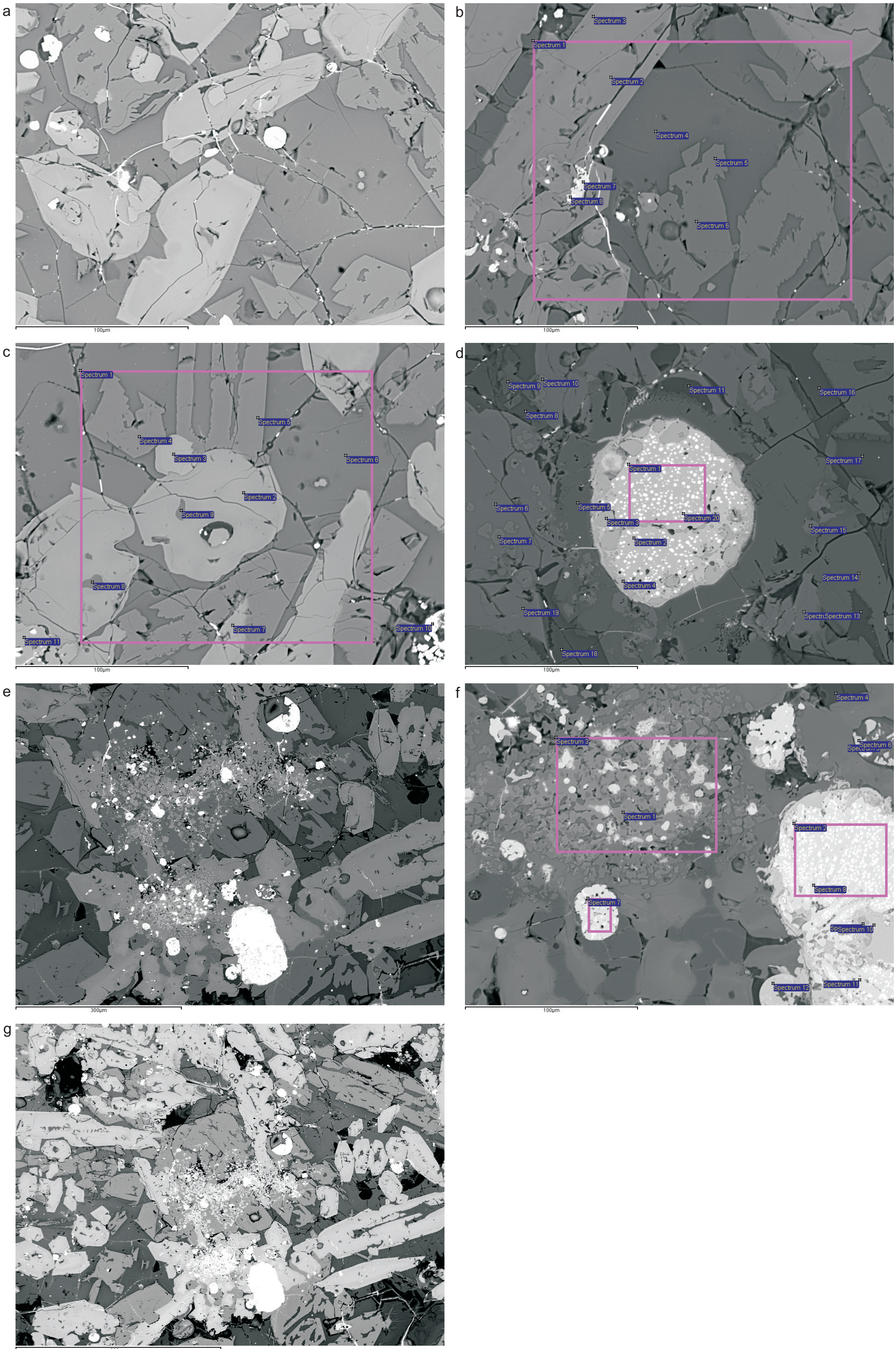

a
Spectrum 7
Spectrum 9
Spectrum 1
Spectrum 2
Spectrum 10
Spectrum 11
Spectrum 3
Spectrum 8
80µm
b
Spectrum 8
Spectrum 10
Spectrum 4
Spectrum 1
Spectrum 11
Spectrum 5
Spectrum 3
Spectrum 2
Spectrum 7
200µm
c
Spectrum 15
Spectrum 9
Spectrum 10
Spectrum 8
Spectrum 6
Spectrum 13
Spectrum 12
Spectrum 5
Spectrum 4
Spectrum 2
Spectrum 1
Spectrum 11
Spectrum 3
Spectrum 14
Spectrum 7
100µm
d
Spectrum 8
Spectrum 4
Spectrum 5
Spectrum 7
Spectrum 3
Spectrum 2
Spectrum 1
Spectrum 6
Spectrum 9
60µm

Plate 9



a
100µm
b
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
100µm
c
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
Spectrum 10
Spectrum 11
100µm
d
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
Spectrum 10
Spectrum 11
Spectrum 13
Spectrum 14
Spectrum 15
Spectrum 16
Spectrum 17
Spectrum 18
Spectrum 20
100µm
e
300µm
f
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 10
Spectrum 11
Spectrum 12
100µm
g
600µm

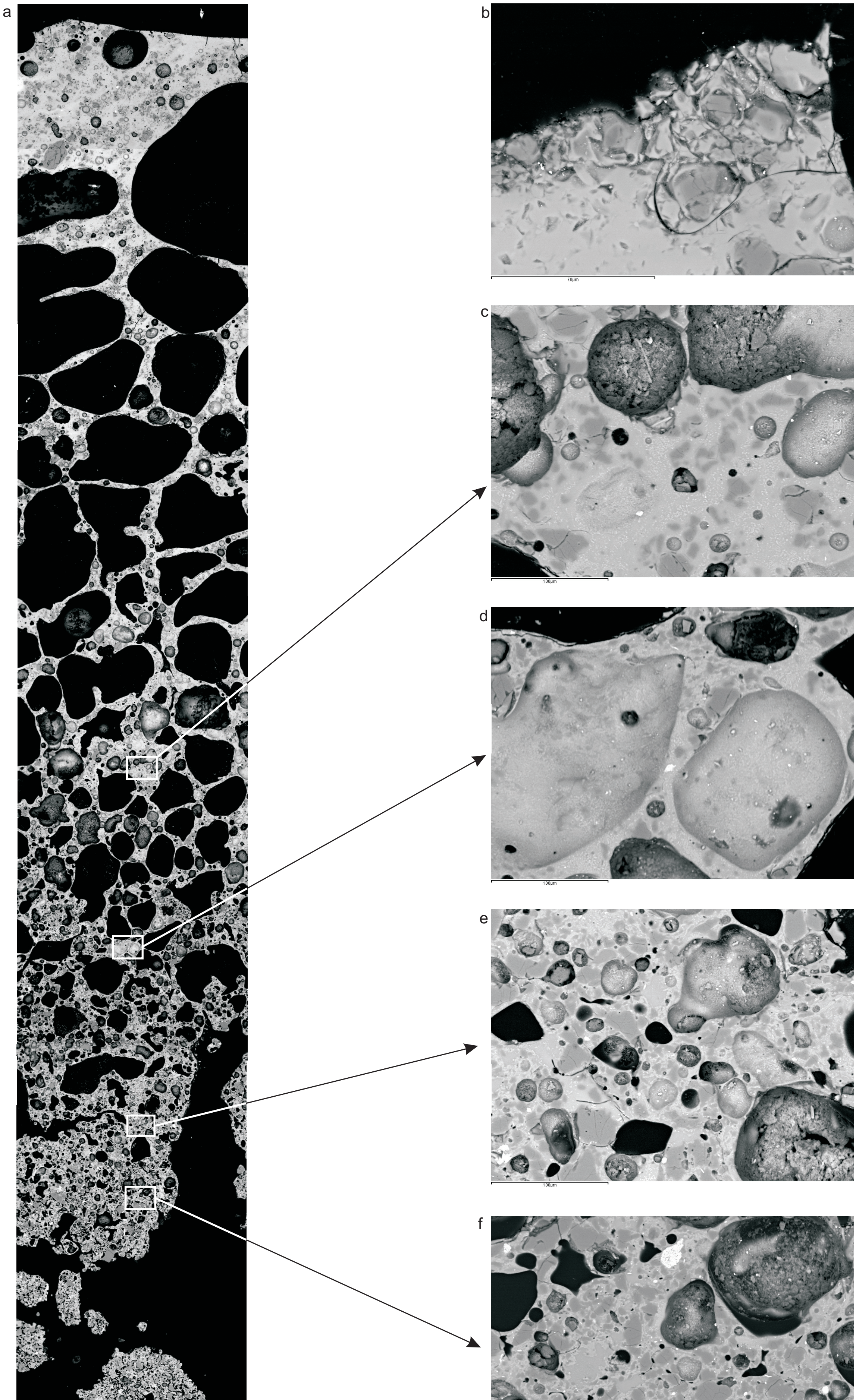

a
b
c
d
e
f

Plate 11

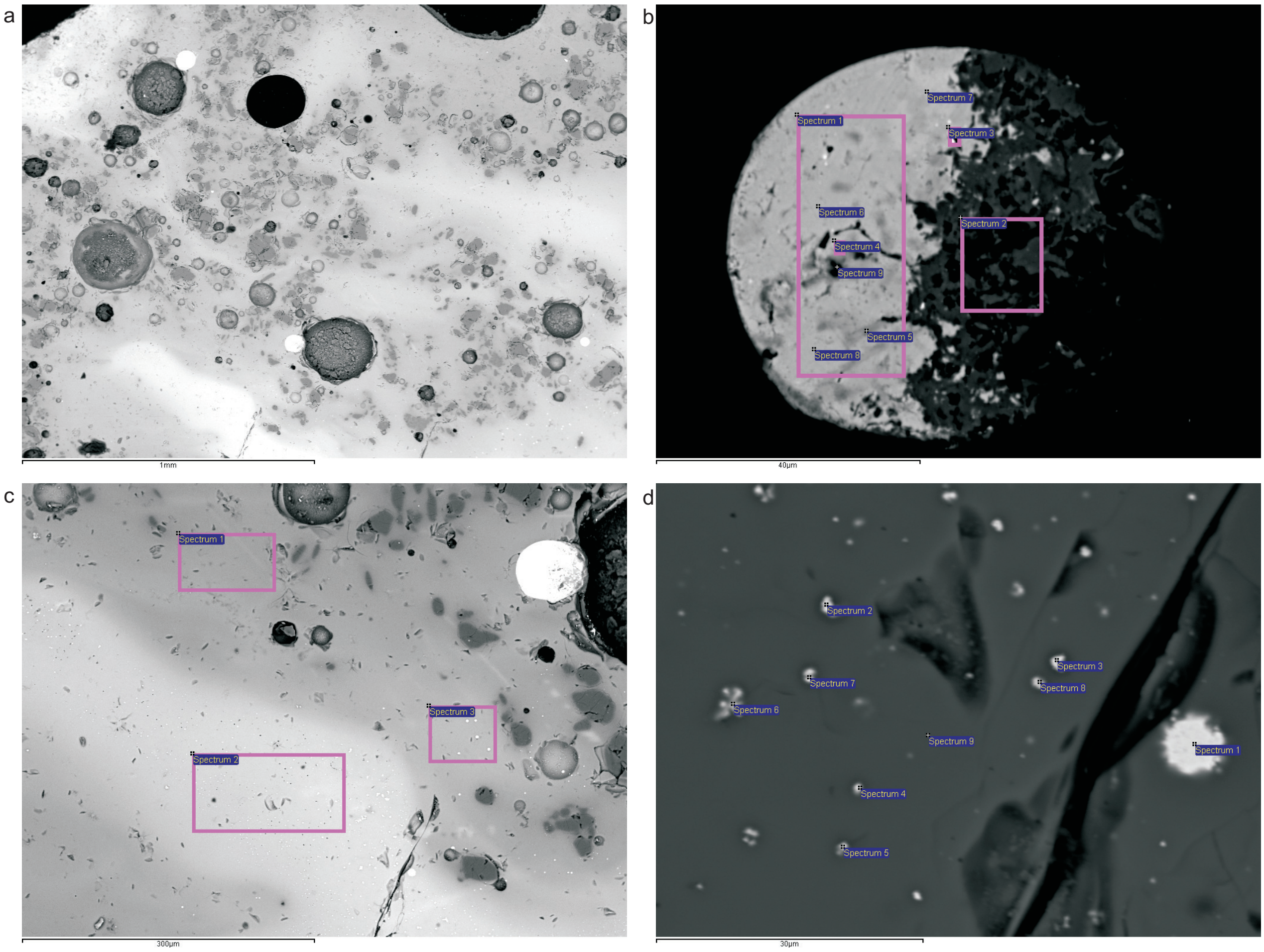

a
1mm
b
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
40µm
c
Spectrum 1
Spectrum 2
Spectrum 3
300µm
d
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
Spectrum 8
Spectrum 9
30µm

Plate 12

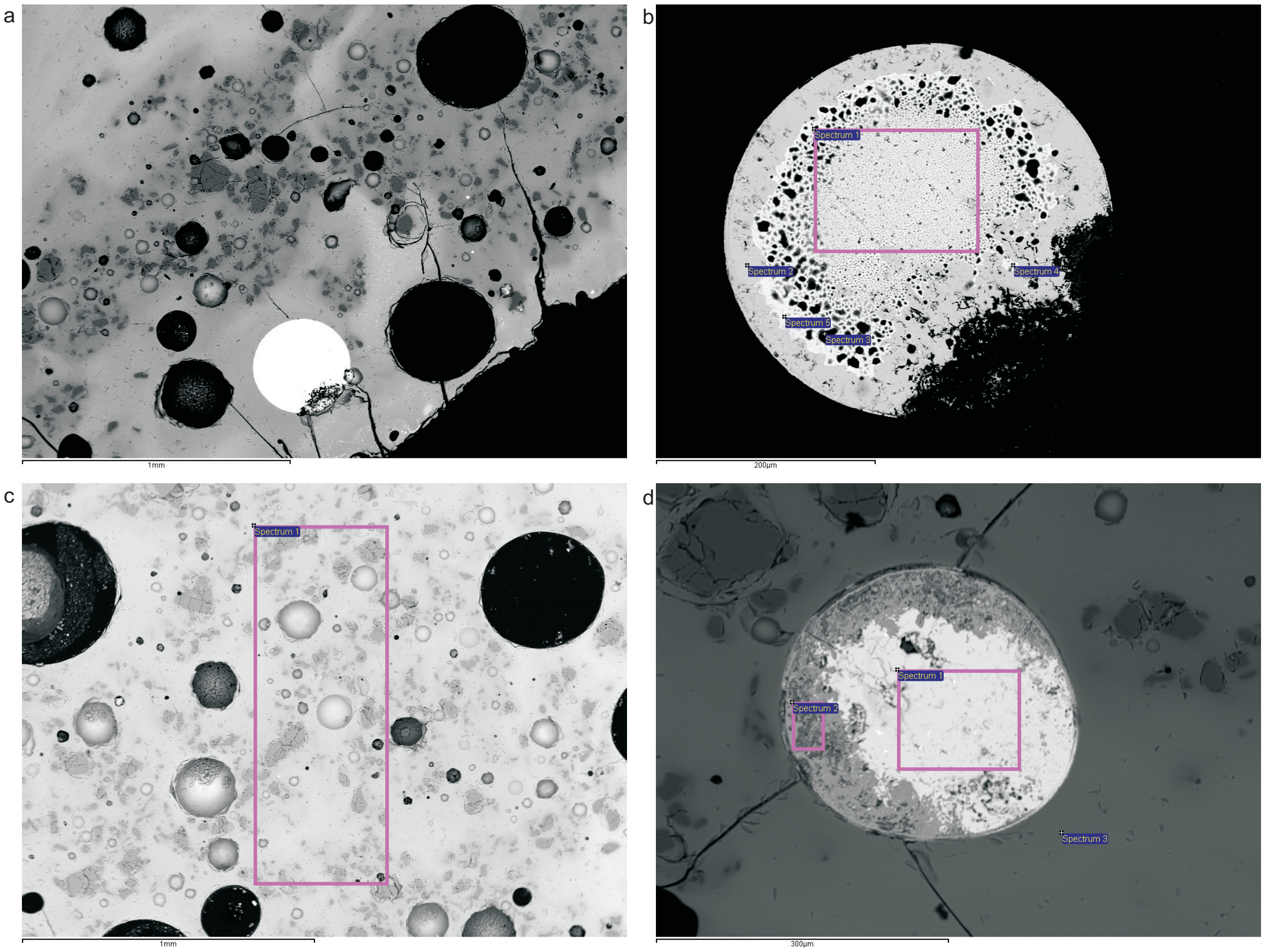
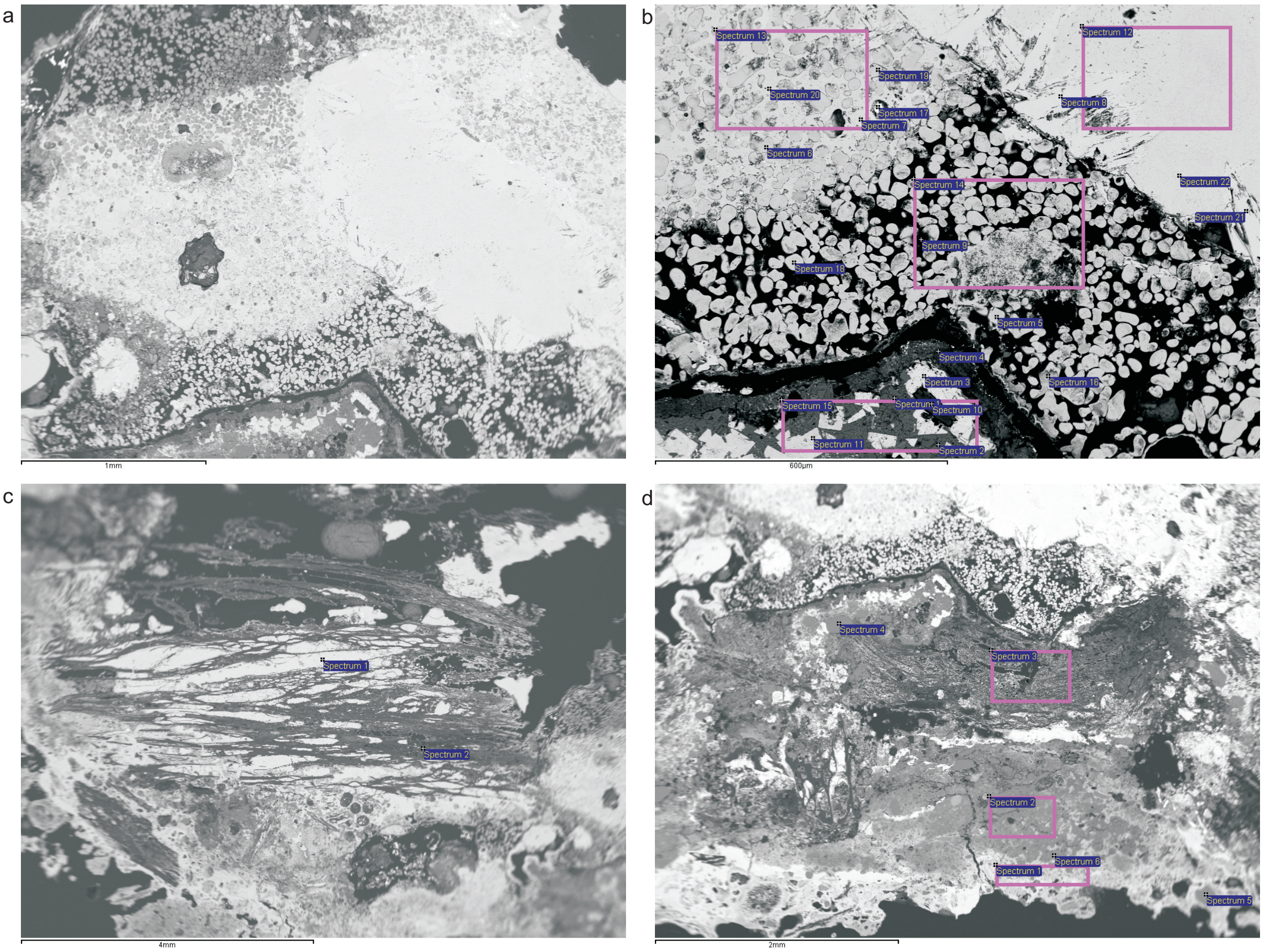

a
1mm
b
Spectrum 1
Spectrum 2
Spectrum 4
Spectrum 5
Spectrum 3
200µm
c
Spectrum 1
1mm
d
Spectrum 1
Spectrum 2
Spectrum 3
300µm

Plate 13


a
1mm
b
Spectrum 13
Spectrum 20
Spectrum 19
Spectrum 17
Spectrum 7
Spectrum 6
Spectrum 12
Spectrum 8
Spectrum 14
Spectrum 9
Spectrum 22
Spectrum 21
Spectrum 5
Spectrum 4
Spectrum 3
Spectrum 15
Spectrum 10
Spectrum 11
Spectrum 2
600µm
c
Spectrum 1
Spectrum 2
4mm
d
Spectrum 4
Spectrum 3
Spectrum 2
Spectrum 6
Spectrum 1
Spectrum 5
2mm

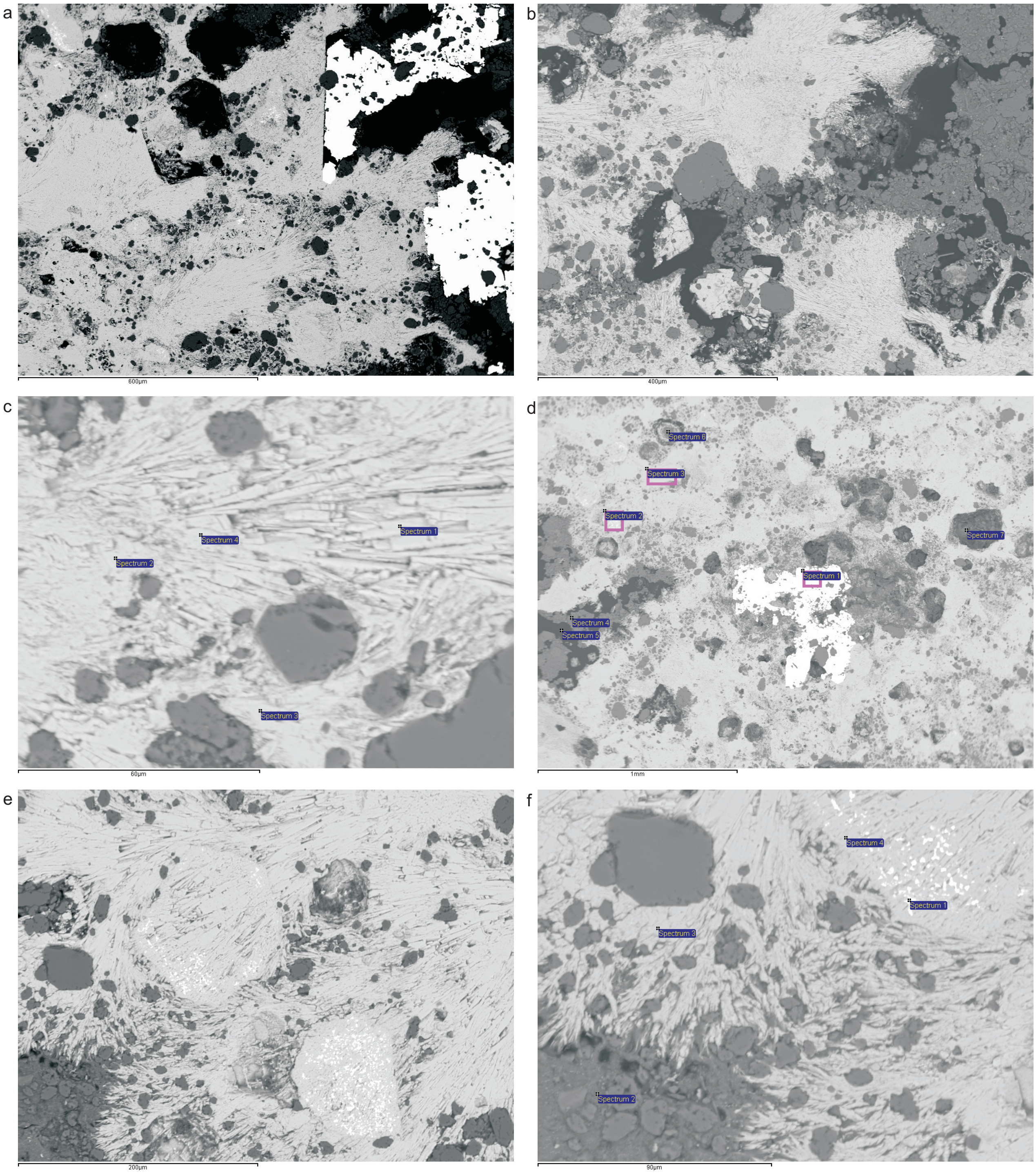

a
600µm
b
400µm
c
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
60µm
d
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
Spectrum 5
Spectrum 6
Spectrum 7
1mm
e
200µm
f
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 4
90µm

Plate 15

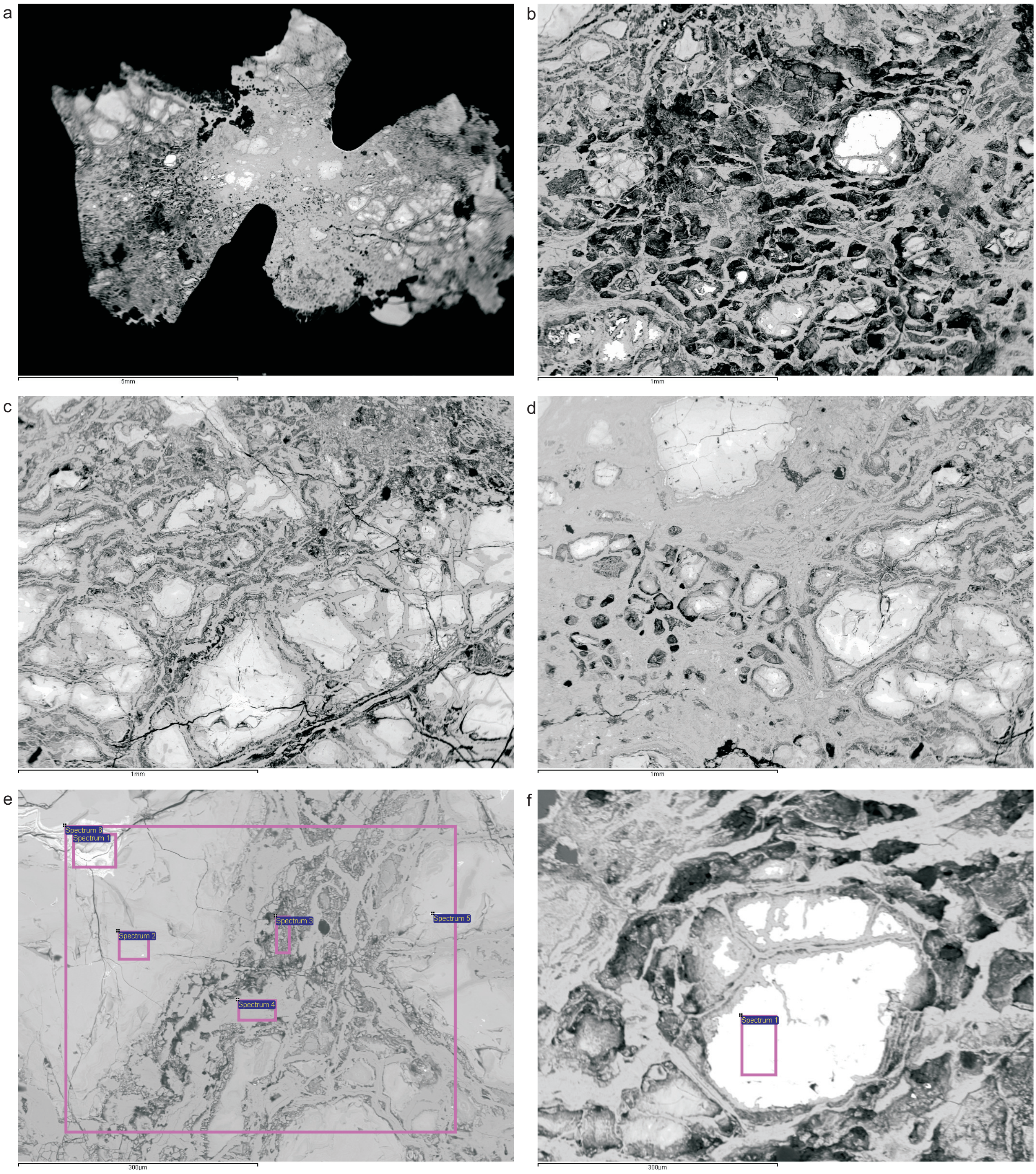
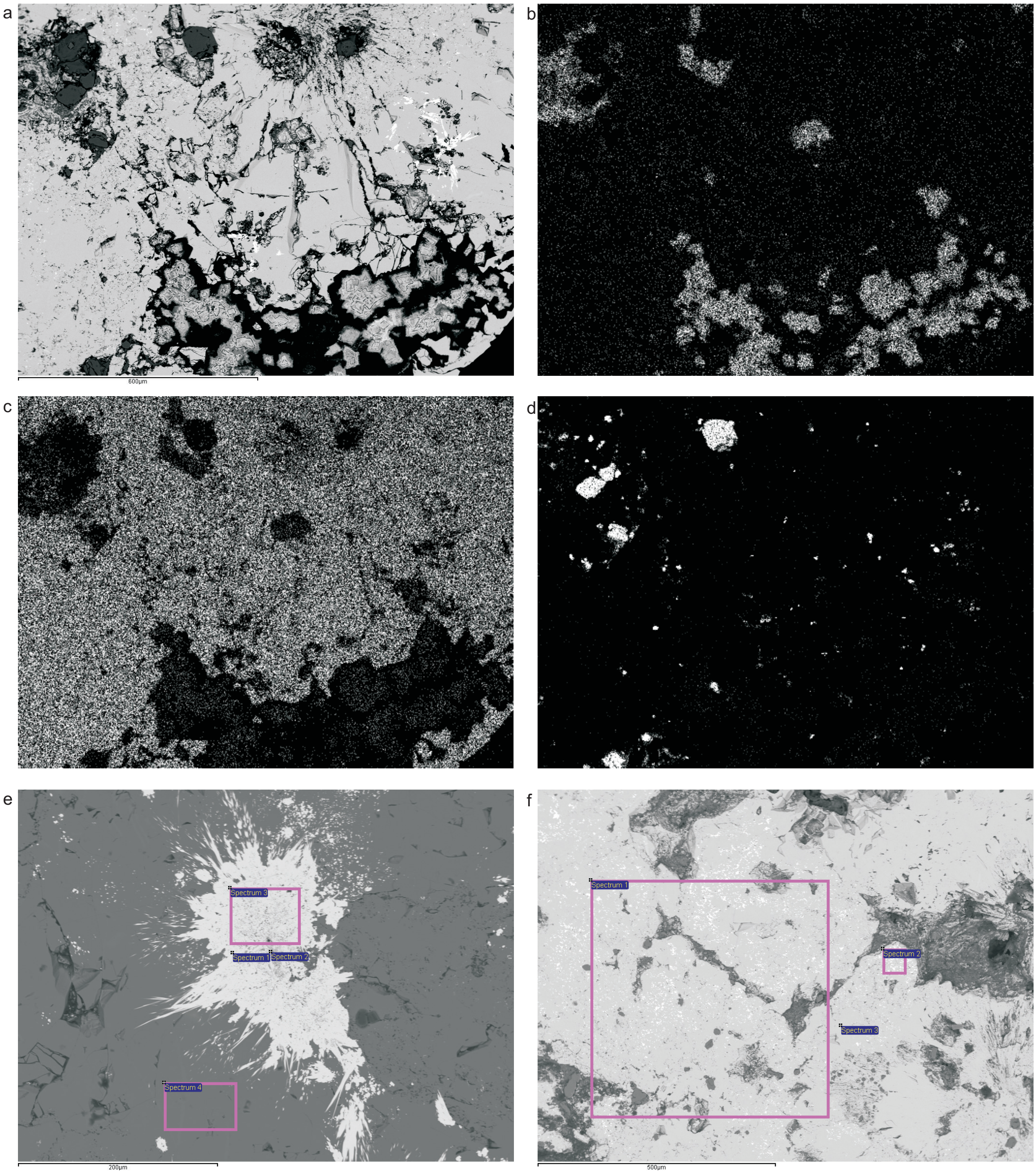
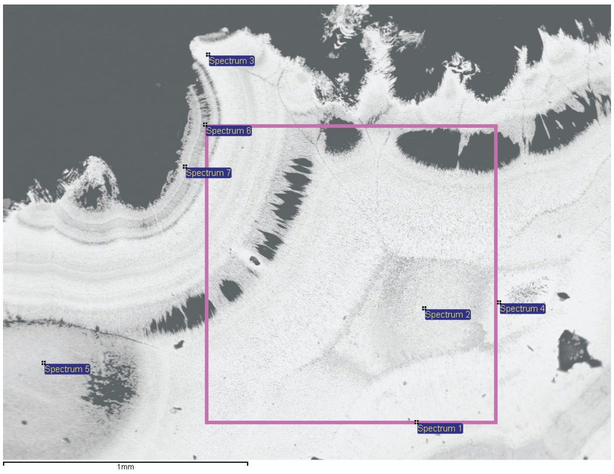

a
5mm
b
1mm
c
1mm
d
1mm
e
Spectrum 6
Spectrum 1
Spectrum 2
Spectrum 3
Spectrum 5
Spectrum 4
300µm
f
Spectrum 1
300µm

Plate 16


a
b
c
d
e
f
600µm
Spectrum 3
Spectrum 1
Spectrum 2
Spectrum 4
200µm
Spectrum 1
Spectrum 2
Spectrum 3
500µm

a


Spectrum 3
Spectrum 6
Spectrum 7
Spectrum 2
Spectrum 4
Spectrum 5
Spectrum 1
1mm

b

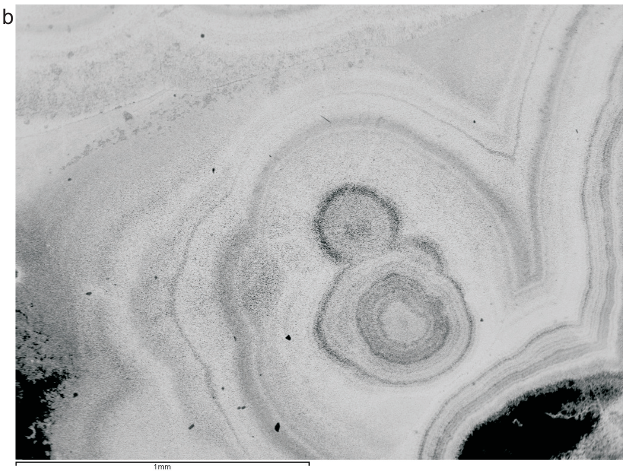

1mm

Plate 18

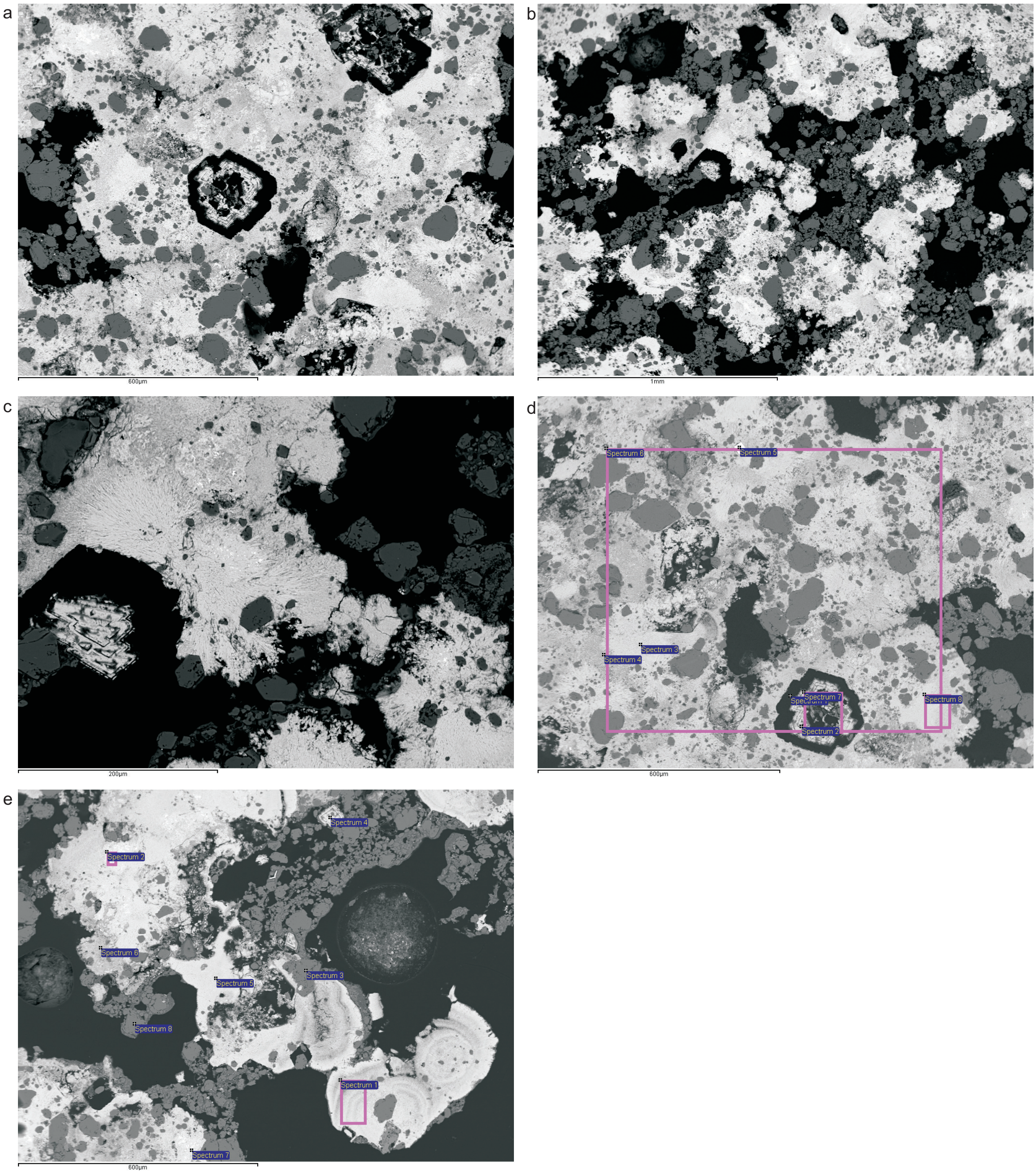
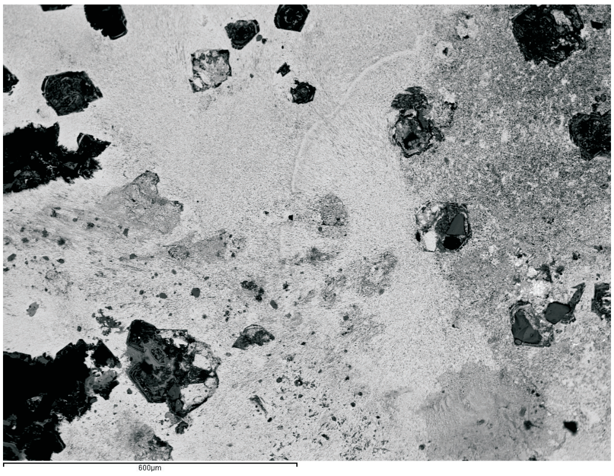
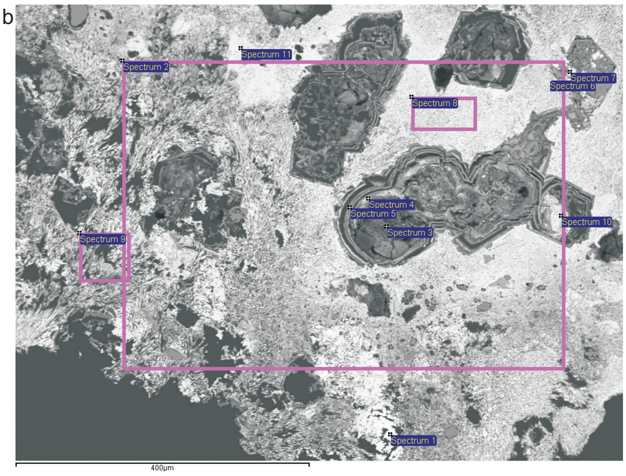

a
600µm
b
1mm
c
200µm
d
Spectrum 6
Spectrum 5
Spectrum 3
Spectrum 4
Spectrum 7
Spectrum 1
Spectrum 2
Spectrum 8
600µm
e
Spectrum 4
Spectrum 2
Spectrum 6
Spectrum 5
Spectrum 3
Spectrum 8
Spectrum 1
Spectrum 7
600µm

Plate 19

a


600µm

b


Spectrum 2
Spectrum 11
Spectrum 8
Spectrum 7
Spectrum 6
Spectrum 4
Spectrum 5
Spectrum 3
Spectrum 10
Spectrum 9
Spectrum 1
400µm

GeoArch

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