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Archaeometallurgical residues from
Ynysfach Ironworks, Merthyr Tydfil

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Abstract

This report describes archaeometallurgical residues during excavations of the Ynysfach Ironworks. The residues were produced during a wide range of metallurgical activities.

The focus of the study is the characterisation and interpretation of residues from the refining of iron in refinery furnaces. The refinery process entailed the remelting of pig iron under strongly oxidising conditions, which were maintained for a considerable time. The iron was tapped and quenched to produce finers metal for feeding the puddling furnaces. The slags from this process have elevated levels of those elements reduced in the blast furnace with the iron – particularly phosphorus, manganese, vanadium and chromium. The elevated phosphorus (up to 6.9wt% P_2O_5) and low calcium (less than 0.6wt% CaO in most specimens) has produced a highly unusual slag mineralogy with phosphoran varieties of the minerals olivine and iscorite, together with a variety of less volumetrically significant phosphatic phases. Vanadium and chromium are concentrated, with titanium and aluminium, in spinels. It is argued that the reduction in the phosphorus content of the iron may have been a major reason for the requirement for the refinery process prior to puddling with Cort's original 'dry' process.

One sample showed a higher silica to alumina ratio and a higher sulphur content than the suite of refinery slags and may possibly be a puddling slag. Puddling was not undertaken at Ynysfach, so if from puddling, this slag is likely to be a residue from the main Cyfarthfa site.

As well as the macroscopic slag flows, the refinery process produced micro-residues of two types: small (<40 μ m) dense spheroids of iron or iron oxide and larger, 100-2500 μ m diameter, hollow spheroids of slag comprising magnetite dendrites in a glass or micro-crystalline matrix. The spheroids were probably generated by the turbulence of the air blast on the molten iron and slag in the refinery furnace respectively. The spheroids form a major component of the deposits in the site's many drains.

The site also produced residues from primary smelting, including both slag and pig iron. Analysis of smelting slags focused on some substantial slag flows that were often associated with iron. Most of the sampled blast furnace slags proved to have an almost optimal composition that appears unlikely to have been attained in the early 19th century. The blast furnace slags may therefore have been discarded on the site at a later date, although the composition of iron inclusions suggests this must have pre-dated the steelworks phase of the Cyfarthfa works.

More certainly from the post-1884 steelworks phase are examples of tuyères from Bessemer converters. Pillow-like masses of viscous siliceous manganese-rich slag are also interpreted as residues from the acid Bessemer process. Two analysed pigs of cast iron were also of 'acid Bessemer' grade. These materials must have been discarded from elsewhere, probably from the main Cyfarthfa site, which undertook Bessemer steelmaking from 1885 to 1910 and again between 1915 and 1919.

The history of the refinery process is reviewed in the light of the new information and contemporary understanding of the process is also discussed.

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1. Methods

All archaeometallurgical materials from the project were examined visually (with a low-powered binocular microscope where required) and the summary catalogue of examined material was presented by Young (2013, Table 1). The material included a range of iron-making and iron-working residues, including blast furnace slags, pigs of iron, refining slags, tuyères from Bessemer converters together with a variety of other materials not identifiable at the assessment stage. The analytical phase of the project was designed primarily to shed light on the refining process, with the investigation of other materials a secondary objective.

A total of 32 samples were taken forward for further analysis (Table 1).

The selected solid samples were slabbed on a diamond saw and subsamples used firstly for preparing a polished block for use on the SEM and secondly for crushing for preparation of a whole-sample chemical analysis. Particulate samples were washed and sieved at 63µm to remove dust before preparation of strew mounts. Polished blocks for investigation on the SEM were prepared in the Earth Science Department, The Open University. Electron microscopy was undertaken on the LEO S360 analytical electron microscope in the School of Earth and Ocean Sciences, Cardiff University. Microanalysis was undertaken using the system's Oxford Instruments INCA ENERGY energy-dispersive x-ray analysis system (EDS).

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 a fused bead 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 thirty six minor and trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U) were undertaken using a sample in solution on the ThermoElemental X-series Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) in the School of Earth and Ocean Sciences, Cardiff University (this also generates lower quality results for Fe, Mn, Ti, P that are used mainly for QA purposes).

The results of the chemical analyses are presented in Table 2 (major elements by XRF) and Table 3 (trace elements by ICP-MS), which are repeated in the Appendix Archive as Tables A1 and A3 respectively). The lower quality analyses are present in Appendix A as Tables A2 (trace elements by XRF) and A4 (major elements by ICP-MS).

Locations of EDS analyses are presented as sample-area-analysis (e.g. NTH2 SOI2 #3). The area of the sample in a particular image is referred to as SOIn (SOI = **Site Of Interest** in the terminology of the INCA microanalysis software) and individual analyses (points or areas) are labelled #m. The microanalytical data are presented in Appendix B, Table B1. Images of all SOIs are included in Appendix C, including, where appropriate, details of the analysed points/areas.

All EDS analyses were collected with all elements analysed (including oxygen, but not carbon; all samples were carbon-coated). Analytical totals were frequently far from 100%, because the analytical system is designed to provide totals of 100% from spot analyses in the centre of the field. The area analyses required for this project are not standardised in the same way and will diverge from a total of 100% (either above or below, depending on the location of the area with respect to the centre of the field). In order to make the microanalytical results simply comparable across

materials (and also sites), no attempt has been made to adjust for the oxidation state of elements with variable valency. The figures employed in the report have therefore been constructed with elements expressed as oxides in weight% calculated stoichiometrically, except for mineral structure calculations, where the measured oxygen has been used.

Examination of samples of iron have been undertaken solely by SEM. Although estimates of carbon content have been made, instrumental determination was not made because the samples were carbon-coated. For ease of comparison analyses of other elements are normalised to 100% for the discussion of iron analyses.

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.

This report is formatted in two sections: the main report is followed by appendices for the archiving of the analytical data.

This project was commissioned by Rowena Hart, of the Glamorgan-Gwent Archaeological Trust.

2. Results

2.a. Distribution of materials

The Ynysfach site, along with many other industrial metallurgical sites, provided very few opportunities for primary incorporation of archaeometallurgical residues into the archaeological record.

The refinery area was largely founded on a deposit of pre-existing blast furnace slag. This deposit was repeatedly disturbed by the construction, rebuilding and removal of various drains and other features. The required formation level for the construction work did not require excavation into the pre-refinery dumps. After abandonment of the site (though whether pre- or post-demolition is unclear) waste from a steelworks, presumably that at Cyfarthfa, was dumped on the site. The widespread robbing of metalwork from the site during the 20th century demolition (including the refinery troughs, cisterns, furnaces, blast pipes etc.) also generated further, often cryptic, disturbance. The level of preservation of the refinery building was slightly below the operational floor level.

The original metallurgical processes were undertaken in upstanding furnaces, which are now truncated. The opportunity for macroscopic slag to occur in primary contexts within the refinery is very limited. The discovery of a slag flow *in situ* within drain [236] (see sample YSF5; Figure 5c), apparently as a result of accidental flowage into the drain, provided a unique opportunity to link the slag-type with the process with a high degree of certainty. The cooling of this flow within a watery drain did, however, produce textures and a chemical composition slightly different to those of flows of slag from the refinery furnace which cooled where intended.

Drains and other structural settings also allowed preservation of accumulations of the microresidues from the refinery process. These spheroids formed in the turbulent environment of the hearth and were carried by the hot gasses, steam and cooling water into all parts of the site refinery area.

In view of all these issues, the decision was made to investigate the better preserved, or more complete, residue pieces, whatever their originating stratigraphic context. The difficulty in recovering residues from primary locations (and thus necessitating the collection of samples from less desirable contexts) is not just one challenging the archaeologist of industrial works, but also the contemporary metallurgical scientist; in 1864 Percy wrote:

'Formerly the cinder was allowed to flow into a cavity in front of the cinder-fall, from which it was taken out at intervals The convenient arrangement of cinder-tubs is now generally adopted. ... It is now possible to keep the front part of the furnace clear and in good order, which could not be done under the old system. I was remarkably struck with the beautiful order of the furnaces at Cyfartha (sic), where the cinder is removed in tubs. I tried in vain for some time to procure, near the furnaces, a small specimen of cinder to carry off as an illustration.'

2.b. Description of materials: blast furnace slags

General

Seven specimens of blast furnace slags were selected for further investigation. One of these (YSF17) was from the same flow as iron sample YSF18. Four samples were from flows (YSF19, YSF20, YSF21, YSF22) with varying proportions of glass and crystalline material (YSF19 a dominantly glassy flow; YSF20 small fragment with a clear glassy top; YSF21 a grey stony flow; YSF22 a similar grey stony flow). The flows from YSF17, YSF19, YSF21 and YSF22 were all of similar cross-sections to iron pigs or their feeders. Thus these samples are interpreted as slag tapped at the end of the tapping of iron; normal slag tapping would have been directly into wagons. Two samples (YSF23 and YSF24) were highly vesicular slags, containing iron clasts. Of these, the prepared sample after mounting for YSF24 showed iron on the polished face (and is therefore 'discussed' in the iron section above).

Mineralogy

The mineralogy of blast furnace slags has been surprisingly little described, even for modern materials. In four (YSF19, YSF21, YSF22, YSF23) of the five examples for which the microstructure was examined, the primary mineral is a melilite, with a composition equivalent to approximately 59-67% åkermanite (Table 4; Figure 2c-f). The fifth sample (YSF17; Figure 2a,b) has primary pseudowollastonite (or one of its polymorphs; Table 1). For the samples containing melilite, the outer part of the melilite shows a cotectic with a very fine sulphide mineral. This sulphide, along with the abundant sulphide blebs in the interstitial areas, appears to be a Fe-Mn sulphide, typically (apart from in YSF23) with a low (10-20%) ratio of Fe:Mn. This contrasts with most published examples of blast furnace slags in which the sulphide in the cotectic with melilite is oldhamite, a calcium sulphide. The sample bearing pseudowollastonite shows a dominantly iron sulphide, with a low proportion of manganese sulphide, and possibly in some case representing incompletely sulphidised iron droplets. All five samples show an aluminous pyroxene as a secondary silicate phase (Table 1). In the case of the sample with primary pseudowollastonite this appears to be a fassaite, but for the others it is of aluminous magnesian (enstatite) composition. The occurrence of aluminous pyroxenes in conjunction with melilite has been discussed by Butler (1977) for modern blast furnace slags from Corby steelworks. Remaining interstitial space is occupied by a glass.

Chemistry

Six of the blast furnace slags (YSF19, 20, 21, 22, 23, 24) show very similar chemical compositions (Table 5), but the seventh (YSF17), differs in many respects:

- it has a high iron content (The XRF sample gave 11.5wt% total iron quoted as FeO, possibly indicating an iron clast was included in the sample; the EDS determinations provided a still elevated, but lower estimate of 2.60wt% iron quoted as FeO on average), whereas the others are much lower (all less than 2.5wt% FeO measured by XRF or less than 0.65wt% FeO by EDS).
- it has a low magnesia:lime ratio (0.7), the others all have a much higher ratio (0.23-0.35)
- it has a low total of lime and magnesia (34 wt%), the others are in the range 38-44wt%

- it has a slightly elevated manganese content (1.95wt% quoted as MnO), the others have less than 1.48wt%

- it has a higher silica to alumina ratio (3.36) than the others, which lie in the range 2.20 - 2.48.

- it has a higher phosphate content (0.42 wt% P₂O₅), the rest have <0.12wt%

The main group of samples (YSF19, 20, 21, 22, 23, 24) have compositions that are very magnesian (8.5 to 10.4wt% MgO).

The upper crust normalised REE profiles (Figure 1) for the samples YSF19,20,21,23,24 are very tightly clustered (total REE 157-287 ppm). They show an elevated middle REE section (MREE), with peaks at Eu and Dy. YSF17 also has moderately elevated REE (total REE of 273ppm), but has a somewhat flatter profile.

Sample YSF22 also shows a flatter, less elevated profile, than the other blast furnace slags.

Sample details

YSF17 (Figure 2a-b; Plates C39, C40)

This sample is taken from a composite flow, 160mm wide and 70mm deep. The top is marked by glassy slag thrown into sharp arcuate ridges. The base is largely obscured by accretion.

The sample is moderately vesicular. The primary phase is formed by elongate crystals of pseudowollastonite (β -CaSiO₃; or one of its polymorphs) with Mg/(Mg+Ca) ~ 0.02, up to 1mm in length and 100µm in width. The wollastonite is followed by interstitial fassaite (Mg/(Mg+Ca) ~ 0.15) compositionally similar (but not identical, being rather more magnesian) to the fassaite described from modern blast furnace slags by Butler (1977) and forming dendritic and mesh-like growths in the wollastonite interstices. The fassaite locally overgrows angular grains (up to 25µm) of FeS bearing 1 µm diameter prills of iron. The fassaite has an interstitial glass which contains blebs of Fe-Mn sulphide, often forming a rim to the fassaite crystals. The sulphide blebs are too small for accurate analysis, but appear to have Fe:Mn typically in a ratio of 96:4 and also frequently appear to show an excess of iron over sulphide, suggesting they may be only partially sulphidised droplets.

This slag formed the upper section of a runner (probably the end of a pig-tapping), for which the basal iron component was samples as YSF18 – a grey cast iron with an abundance of manganese sulphide inclusions.

YSF19 (Figure 2c-d; Plate C42)

This specimen is the margin of a flow. The interior is pale grey and crystalline; the exterior is a grey-green glass, more brightly pale green at the contact with the crystalline interior. The outside is strongly flow folded, there are large internal cavities of irregular form. The base is a pale green glass, forming prills descending between coke fragments. The whole has an incomplete profile, but the part surviving is lenticular, suggesting a flow 140mm wide and 80mm thick.

The primary phase in this sample is a melilite (Mg/(Mg+Ca) ~ 0.23; approximately 60-63% åkermanite), forming approximately 90% by volume. The outer margins of the melilite form a cotectic with a very fine-grained sulphide mineral, probably a manganese sulphide. The interstitial area contains a rather vesicular glass, with abundant manganese sulphide prills and droplets (some with a hollow form). The interstitial glass also bears some unidentified

crystallites, including one with a similar electron density to the aluminous enstatite in YSF21-23, but also including a potassium-bearing phase.

YSF20 (chemical analysis only)

A small fragment from the margin (top?) of a slag flow. The interior is a pale grey slag, with a slightly brownish surface where seen in side large convoluted cavities. The external surface is a slightly greenish grey glass, becoming a more vivid pale green near the contact with the crystalline interior.

YSF21 (Figure 2e-f; Plates C43, C44)

The specimen is a ropey-surfaced flow of at least 200mm width, and with, apparently, a rather convex upper surface. The flow was broken and the fragment heavily accreted onto other slag fragments.

This specimen is very similar to YSF19, with a main primary phase of melilite ($Mg/(Mg+Ca) \sim 0.23$; approximately 61-67% åkermanite). The melilite shows a cotectic relationship to manganese sulphide on its margins. A minor, stubby, angular dendritic phase, is interstitial to the melilite and appears to be an aluminous magnesian pyroxene, broadly comparable to an aluminous enstatite. This is better developed than the interstitial phase in YSF19, in which the interstitial regions are dominantly glass, but they are likely to be the same. Further blebs of Fe-Mn sulphide (with less than Fe:Mn <0.2) occur within the interstitial glass, particularly along the margins of the melilite.

YSF22 (Figure 2g-h; Plate C45)

This specimen was taken from a grey stony slag flow, 250mm in width and 80mm deep. The top has a ropey flow surface of arcuate ridges. The base is rough with inclusions of coke. The slag is finely vesicular in places, probably picking out flow lobes. There are no glassy margins.

This specimen is broadly mineralogically similar to YSF21, with primary melilite ($Mg/(Mg+Ca) \sim 0.23$; approximately 61-64% åkermanite) with a very minor development of a marginal cotectic with Fe-Mn sulphides (Fe:Mn = 0.11-0.21), followed by interstitial glass with finely dendritic aluminous enstatite and further sulphide blebs. The difference is the dominance of the angular melilite dendrites and the very reduced interstitial areas.

YSF23 (Figure 2 a-c; Plate C46)

This specimen has a layered structure, with a basal (?) layer of up to 10mm of fine homogeneous grey slag. Above this a slightly vesicular horizon about 5mm thick marks the appearance of slightly browner slag, which becomes less vesicular for 8mm, then rapidly more coarsely vesicular, over 50mm the vesicles increase in size from less than 1mm to over 100mm, giving a frothy, pumiceous texture.

This specimen is much finer-grained than YSF21 and 22, but of similar mineralogy where crystalline. The very fine, elongate melilite dendrites grade into regions of glass. The melilite is of similar composition ($Mg/(Mg+Ca) \sim 0.24$; approximately 59-60% åkermanite) as is the subsequent minor aluminous enstatite. The interstitial blebs of Fe-Mn sulphides are slightly more iron-rich (Fe:Mn of 0.32-0.49). The specimen also has some unusual rounded pores, the surface of which is covered by a meshwork of Fe-Mn sulphide (Fe:Mn of 0.30), apparently containing small grains of iron.

YSF24 (chemical analysis only)

This piece was an irregular fragment of frothy slag, bearing prominent iron clasts. Where seen fresh, the slag resembles the upper part of YSF23, being a pale grey slag with large

rounded vesicles. Elsewhere the slag is very rusty because of the corroded iron inclusions.

The prepared sample proved to not have slag on the polished face, which was entirely grey cast iron. The SEM investigation therefore appears under 'iron' (below).

Discussion

The slags YSF19, 20, 21, 22, 23, 24 for a fairly coherent group of analyses, at least for the major elements (notwithstanding the different REE profile for YSF22). They are indicative of the use of a dolomitic limestone as flux, or, less likely, a very magnesian iron ore. The general composition suggests that this group represents slags produced from a repeated smelting 'recipe' (although the REE evidence may suggest a different source for at least one of the components of YSF22),.

Plotting the analyses of this group of slags on the SiO_2 -CaO-MgO pseudoternary diagram, for an Al_2O_3 component of 15% (Figure 3; fields after Muan & Osborn 1963, figure 113), shows that they lie on a trend precisely aligned on the lowest possible SiO_2 content for a slag in this system that is liquid at 1500C (a typical blast furnace slag temperature). This location is important for it will correspond to the most highly desulphidising slag composition. This is a slag composition that is highly unlikely to be present here except by design.

This type of slag composition is not documented in historical accounts of iron smelting in Merthyr Tydfil. The Merthyr Tydfil ironworks of the late 18th to mid 19th century relied almost entirely on fluxes taken from the Dowlais Limestone Formation (Cil-yr-ychen Limestone) – from Twynau gwynion for Dowlais until 1825, Morlais Quarries East for Dowlais after 1825, Morlais Quarries West for Penydarren and Gurnos quarries for Cyfarthfa. At none of these quarries is the limestone significantly dolomitised. The influence of the Dowlais Limestone Formation may be illustrated by analyses of slags from Dowlais ironworks in the 1850s provided by Percy (1864, p.499). These analyses are not necessarily as accurate as modern ones, but the slags show low magnesium (with one exception) supporting the expected slag composition from the use of the Dowlais Limestone.

Of this group of slags, just one is directly associated with an iron sample, YSF24. This was a small iron prill caught up in the highly vesicular slag, so may not necessarily be representative of the iron produced, but was a rather phosphoric grey cast iron, with medium sulphur and silicon.

2.c. Description of materials: iron

General

Five samples of cast iron were taken, and one sample taken to examine a blast furnace slag proved to only show cast iron on the polished mount.

One of the samples (YSF13) was taken as a possible finers metal sample, one was a gutter-shaped runner or failed pig fragment from a context below a wall of the refinery (YSF14), two were fragments from pigs (YSF15 and 16), one was from a runner with pig iron below glassy slag (YSF18) and one was an iron inclusion with a frothy blast furnace slag.

Chemistry

The chemical composition of the samples (Table 6) was rather variable. For two samples (YSF15 and YSF16) levels of phosphorus, silicon, sulphur and titanium were only infrequently above the detection level. These two samples had silicon at about 2.4wt% (EDS analyses normalised to 100% excluding carbon) for YSF16 and 2.6% for YSF15. Manganese was present at 0.80 and 1.10% for YSF15 and YSF16 respectively.

Analyses of all the other examples showed detectable quantities of phosphorus and sulphur.

Sample YSF18, demonstrably an end-of-tap iron run, showed very high levels of manganese and sulphur (together totalling over 11wt%), as well as detectable titanium in most analyses. This sample was also the most phosphoric piece, with analyses averaging 1.26wt%, just slightly lower than silicon at 1.38wt%.

The grey cast iron inclusion from with the highly vesicular blast furnace slag (YSF24) had similar levels of silicon (1.24wt%) and only slightly lower phosphorus (0.94wt%) to those of YSF18. The manganese content was moderately high (0.89wt%), well in excess of that of sulphur (0.26wt%).

The fragment of grey cast iron casting, YSF13, showed levels of manganese (0.66wt%) in excess of those of sulphur (0.33wt%). Phosphorus was moderately high (0.87wt%), with silicon at a rather similar level (0.83wt%).

The single white cast iron fragment (YSF14) has a high silicon content at 2.3wt%, a moderate phosphorus content (0.80wt%) and a rather high sulphur content (0.82wt%), but a very low manganese content (0.14wt%).

Sample details

YSF13 (Figure 4a-b; Plates C33,C34)

Sample YSF13 was taken from a fragment from the margin of a slab of cast iron, 60-65mm thick and thus matching contemporary description of the thickness of the cast slabs of finers metal. The piece proved, however, to be a grey cast iron. It probably represents the margin of the casting.

This specimen is a grey cast iron, with extensive graphite. There is extensive development of steadite and there are abundant inclusions of manganese sulphide (present as angular, euhedral, forms up to approximately 15µm).

YSF14 (Figure 4c-d; Plates C35,C36)

This specimen is from a flow of iron 85mm wide, slightly concavo-convex in profile and 20-25mm thick in the centre.

This sample is a white cast iron with cells (rounded, approximately 50 µm across) of pearlite surrounded by cementite and steadite. There are abundant sulphide inclusions, which are primarily iron sulphide.

YSF15 (Figure 4e; Plate C37)

This sample is from a large iron flow, approximately 140mm wide, slightly concavo-convex in profile and up to 40mm deep. The surviving piece of flow was 550mm in length. The piece bears abundant cavities in the iron, which are apparently original.

This is a grey cast iron, with a very high density of graphite, which shows rapid changes of scale across the specimen. The outlines of the primary austenite are clearly delimited by the dense graphite.

YSF16 (Figure 4f; Plate C38)

This piece was cut from the tip of a pig fragment 620mm long. At the point of section the pig was 80mm wide and 30mm thick with a very slightly convex top.

This possesses a microstructure, similar to that of YSF15, of very dense graphite, with very rapid changes of graphite size across the sample (1mm to 10µm).

YSF18 (Plate C41)

This sample is a grey cast iron, with a rather low proportion of graphite, a high proportion of steadite and a very high density of manganese sulphide inclusions. There are also some titanium nitride inclusions.

The extraordinary density of manganese sulphide is compatible with the likely origin of this sample at the tail-end of a tap, in which the manganese sulphide, which floats in the iron, will become concentrated.

YSF24 (Figure 4g-h; Plate C47)

This sample was a typical grey cast iron. The graphite was large and evenly distributed. There was a moderate concentration of euhedral manganese sulphide inclusions.

Discussion

The interpretation of these materials presents various challenges. Not least of these is the nature of the iron involved. With the exception of casting YSF13, the specimens are what might be termed semi-products – that is to say, materials from within the *chaîne opératoire*. The reason for their deposition on the site is not clear – were these typical materials 'lost' within the works, or substandard materials deliberately discarded?

The iron from the slag-topped runner, YSF18, is clearly waste material, the slaggy end of an iron tapping, rich in the inclusions that would have floated towards the top of the iron in the blast furnace. This iron is highly phosphoric and must therefore predate the conversion of the site to a steelworks.

The same argument could be applied to the other phosphoric pig irons (grey iron YSF24 and white cast iron

YSF14). In contrast, the pigs sampled for YSF15 and YSF16 (both from c194) show low phosphorus and low sulphur, but moderately high manganese and high silicon. These would potentially be identifiable as pig suitable for conversion in an acid Bessemer converter – for which most impurities are typically kept low (Table 7), but the silicon content needs to be kept above 2% in order to provide sufficient heat during the blow (the oxidation of silicon is strongly exothermic and produces much of the heat required for raising the temperature of the metal for the decarburisation phase). The target range for acid Bessemer pig would be 2-3% silicon, less than 0.05% sulphur, less than 0.1% phosphorus and 0.7 to 1.0% manganese (or certainly less than half the concentration of silicon; Forsythe 1909, supplement p.287). These characteristics are met by the observed compositions of YSF15 and YSF16.

The phosphoric grey pig iron (YSF18), since a pig and therefore from primary production, is not likely to be from the steelworks phase (when any phosphoric grey iron would have been handled only in a foundry context). The flow of YSF18 was capped by slag sampled as YSF17. Slag sample YSF17 (see above) was chemically distinct from the other slags, suggesting a different, low magnesium, fluxing material, and was more strongly phosphoric.

Grey iron YSF24 was an inclusion in a slag (see above) which was one of the main group of blast furnace slags (YSF19, 20, 21, 22, 23), but at the compositional limits of that group. It serves, however, to tie at least some of the high magnesium slags to the production of phosphoric grey iron, not pig iron suitable for the acid Bessemer process.

White cast iron YSF14 is problematic. It has a high silicon content which should have promoted graphite formation; that the iron is white, suggests it has been rapidly chilled, inhibiting graphite formation. It has a high phosphorus content, indicating it is not a semi-product from the steelworks era. The sulphur content is high and the manganese content low. These compositional features suggest that material is not finers metal. The most likely interpretation of this piece is probably that it is the chilled piece of cast iron, perhaps an incompletely filled pig (hence the gutter-like form of this piece and of the other iron fragments found with it) or the end of a tap, and it may have been discarded (along with a number of other fragments with which it was found) as being poor iron.

2.d. Description of materials: refinery macro-slags

General

The single occurrence of a refinery slag within a secure context was an *in-situ* flow of slag that had descended into drain [236] (context 307, sample 145). This block is highly and coarsely vesicular (YSF5; Figure 5c), with a flow lobed top. The flow appears to have accidentally penetrated through the drain cover and its vesicular texture is attributed to the water-rich environment of cooling.

Other examples of refinery slags are linked by their chemical composition to the *in-situ* example, but show rather different textures. The most common morphology is to have a lower, dense slag sheet, penetrated by tubular vesicles, which is abruptly overlain by a vesicular upper section (Figure 5a, b). These composite flows are interpreted as indicating partial degassing of the slag after flow, but with some gas (including water vapour from the cooling water injected through the slag in the tubular vesicles) being trapped by the chilled upper surface, leading to a vesicular upper section.

Many of these slag pieces are wedge-shaped (Figure 5a, b). Their flow-lobed to smooth upper surfaces are suggestive of a horizontal orientation, so the bases presumably dipped into a hollow. Accounts of the tapping regime of refineries suggest the slag may have flown down the run-out trough to a pit at the end, but this cannot be confirmed by the current data.

Mineralogy

The mineralogy of the refining slags presents some considerable problems in the identification of all the phases present, because of the high phosphorus content, which has produced a wide range of unusual phosphoran varieties of common slag minerals, as well as some unusual phosphate minerals.

The primary phase in most of the slags was wustite. Analyses of the wustite typically show approximately 1% of manganese, probably present within the wustite itself. Many analyses show detectable levels of aluminium, silicon, titanium, vanadium and chromium; these are perhaps more likely to indicate inclusions of spinel. Perhaps the magnetite formed by exsolution on cooling was able to take up these elements. Wustite was typically only well-preserved where encased in the subsequent olivine; where exposed in the interstices of the olivine it was mostly highly reacted and overgrown by spinels and by iscorite (described in more detail below). Even where completely encased by olivine, the wustite locally showed complete replacement to magnetite.

The volumetrically most important phase in the refining slags is a phosphoran fayalitic olivine (phosphoran olivine was defined by Boesenberg & Hewins 2010 as having greater than 0.03 atoms per formula unit APFU, of phosphorus), with the analyses showing atom% phosphorus of 0.51 to 10.94% (Table 9). This corresponds to a range of 0.04 to 0.75 APFU of phosphorus (Figure 6). Phosphoran fayalite is rare in nature (recorded from just a handful of terrestrial and extra-terrestrial sources; Boesenberg 2006, Goodrich 1984a, 1984b). Most occurrences show only a few percent substitution of phosphorus into the fayalite. Boesenberg and coworkers (2004, 2010, 2012) have managed to synthesise a wide range of compositions of up to 0.7 APFU phosphorus, thereby confirming the structural substitutions involved. Recently Schneider *et al.* (2013) have reported on phosphoran olivine with 0.3 to 0.54 APFU phosphorus from a burnt bone-bearing Iron Age ritual site in Austria. More significantly Boesenberg (2006) reported

phosphoran fayalite in the slag inclusions present in the wrought iron of USS Monitor.

Boesenberg & Hewins (2010) have shown that phosphoran fayalite is a metastable phase, requiring rapid cooling from high temperature to form.

The olivine is dominantly fayalitic, with the olivine cores of most samples (YSF2,3,4,5,8,25,27,29) showing compositions of Fa97-98Fo3-2. The magnesium rapidly disappears outwards (and with rising phosphorus substitution). All olivine found to have more than 0.16 APFU phosphorus was also greater than Fa99.

Manganese substitution in the olivine with lower phosphorus (<0.12 APFU P) is clustered between 4% and 6%. For analyses with more than 0.12 APFU phosphorus, there is a relationship between manganese substitution and phosphorus – with typical values rising from 4.5% substitution at 0.12 APFU to 6.0% at 0.70 APFU phosphorus. This phenomenon may be linked to the texture of the samples (YSF4,9,25, 27) involved, with these examples being generally those recorded as being the denser and less porous examples.

In some (but not all) instances there appears to be a slight compositional break, with the outermost phosphoran olivine, at close to phosphoran end-member composition, lying abruptly on less phosphoran olivine. The outermost parts of the phosphoran olivine may show continuity with laminae extending out into the interstitial space between other phosphate minerals (see further below).

The mid to outer sections of the phosphoran olivine commonly include examples of strongly zoned spinels. The spinels enclosed entirely within the olivine are dominantly hercynite, but are heavily substituted (Figure 7). The cores may be modelled as 31% hercynite with up to 31% chromite, 15% coulsonite, 3% ulvospinel, and 21% magnetite. The core regions show rather rapid drops in chromium and vanadium, so that the outer parts are typically in the range of 68-78% hercynite, with up to 1% chromite, 2-7% coulsonite, 4-8% ulvospinel and 15-19% magnetite.

Where the spinels occur in the interstitial areas, although they show a similar range of compositions, they are typically larger and commonly show sector zonation. The sector zonation is due to variations in titanium, giving alternating regions of 4-8% and 8-17% ulvospinel.

The spinels in the interstitial areas are followed by the development of what is here termed 'phosphoran iscorite' (Figure 8; Table 12). This phase has not been described before, but appears to follow a similar range of substitution of phosphorus for silicon as is observed in phosphoran olivine. The iscorite typically forms as an overgrowth to the altered remnants of wustite dendrites, but may also occur as apparently isolated plates. Its morphology and microstructural relationships precisely parallel that of iscorite ($\text{Fe}^{2+}_5\text{Fe}^{3+}_2\text{SiO}_{10}$) in phosphorus-poor slags. However, the analyses of this phase show a composition varying from 0.33 to 0.81 APFU phosphorus for silicon. A composition with approximately 0.6 APFU phosphorus is most common. There appears to be minor substitution of aluminium (as is typical in normal iscorite) and substitution of about 2% of the Fe^{2+} by Mn^{2+} . No phase of this composition appears to have been described in the literature previously.

In some instances the growth of phosphoran iscorite is associated with the growth of other phosphate minerals (see below). In many cases, the surface of the iscorite bears blebs of iron sulphide (but compare with the more important development of sulphides at this point in the paragenesis in the puddling slags, below).

The last stage of the paragenetic sequence is the formation of a variety of late phosphate-bearing phases. These show complex relationships and very little compositional contrast to aid microstructural investigation. The account below should be considered a provisional account of these very complex materials.

The areas interstitial to the olivines, spinels and iscorite may, if small, sometimes show a single pore-filling phase, of an alkali calcium iron phosphate (Table 10), but more commonly, this mineral produces a laminated pore fill, in combination with other phosphorus-rich phases. This mineral remains unidentified, but appears to have an (unbalanced) empirical formula (by EDS) close to:



with iron as the dominant divalent cation and potassium as the dominant alkali. This mineral shows an elongated section in the laminated structures, suggesting it is tabular. In places, it is clearly earlier than at least some of the phosphoran iscorite. This mineral will be referred to as phosphate mineral 'A' for brevity.

Phosphate mineral 'A' is interlayered with a variety of other phases. Most significantly it may be interlayered with laminae of the phosphoran end-member of the phosphoran fayalite (as described above), usually present as outgrowths from the main olivine crystals. This shows a composition with approximately 0.70 APFU phosphorus (i.e. approximately $\text{Fe}_{1.5}\text{Mn}_{0.10}[\text{Si}_{0.27}\text{P}_{0.70}\text{O}_4]$).

These laminae of phosphoran fayalite commonly include rounded blebs (possibly dendrites) of cotectic iron calcium phosphate (Table 11). This mineral has a composition consistent with being an iron-rich graffonite, with an average composition (by EDS) of:

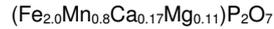


Sample YSF27 shows locally the outermost P-rich phosphoran fayalite to be intergrown both the phosphate mineral 'A' and with a calcium iron phosphate, which appears to form parallel laminae, approximately 3µm thick, within the fayalite. This mineral is more calcium-rich than the graffonite described above, and shows a O:P ratio of greater than four, suggesting it may contain hydroxyls. The small size of these laminae means the quality of the analyses by EDs is poor; this phase will be referred to a phosphate mineral 'B'.

The boundaries between the laminae are frequently demarked by thin developments of iron sulphides, and locally the phosphoran fayalite laminae are replaced in the sequence by material similar in composition to phosphate mineral 'A', but with slightly different elemental proportions, and containing a significant number of sulphide inclusions. It is suspected that this material may be a non-stoichiometric phase.

The interstitial areas bear small amounts of sulphide minerals, mainly present as tiny blebs and filaments the latest phases. Where analysed, these proved to be FeS, sometimes with less than 0.5% of copper.

Some of the material (notably areas of YSF8 and YSF27) show evidence for high temperature alteration after the formation of the primary mineralogy. This was probably driven by hydrothermal processes. In YSF8 (Figure 13 f-h) this takes the form of zones of reaction associated with the vesicles in which the phosphoran fayalite is replaced by a fine mosaic of silica (tridymite?) and an iron oxide (probably magnetite), with a widespread pore-filling complex iron phosphate material of uncertain nature and unbalanced empirical formula of approximately:



The neomorphic iron oxides not only form fine mosaics, but also magnetite rims to the remnant hercynite crystals, often with the texture of the surrounding mosaic apparently strongly influenced by the crystallographic orientation of the iron oxides on the spinel base.

In YSF27 the altered zone (Figure 13a-e), approximately 200µm thick, follows one margin (the basal surface). The progression of textures from inside outwards is:

- Phosphoran fayalite altered with loss of iron and phosphorus
- The altered zone coarsens, so silica-magnetite becomes visible. A much coarser mosaic develops around the hercynite crystals and along olivine grain boundaries
- The outer margin of the mosaic zone may be coarse, with the mosaic in some areas possibly picking out the structure of former olivine.
- An abrupt margin, locally marked by voids and by strong magnetite development on underlying hercynite (total thickness of altered zone is 40-100µm)
- A zone 20-100µm wide of iron phosphate, approximately: $(\text{Fe}_{1.59}\text{Ca}_{0.59}\text{Mn}_{0.35}\text{Mg}_{0.03})(\text{PO}_4)_2$ bearing angular magnetite grains of close to end-member composition.
- An outer rim formed by inward growing large magnetite grains, forming scale-like layer.

Chemical Composition

The refining slags show an unusual, in terms of the chemistry of published historic slags, and potentially characteristic chemical composition (Table 8).

The iron content is moderately high (approximately 61 to 71wt% expressed as FeO). Silica and alumina contents are relatively low (12-17wt% and 2-4.5wt% respectively). The alkalis (soda and potash) and the alkali earths (lime and magnesia) are also all relatively low. Those elements capable of being reduced into the iron during smelting are all present in strongly elevated quantities (manganese, phosphorus, vanadium and chromium). Vanadium is present at up to 5000ppm and chromium to over 2200ppm; manganese (expressed as MnO) and phosphorus (expressed as P_2O_5) reach up to 5.0 and 6.9wt% respectively.

Y, Th, U and the REE are all present in low concentrations. Total REE is 24-67ppm. The U:Th ratio is 0.25 to 0.48.

The Upper Crust normalised REE profiles (Figure 9) are irregularly humped. Samples with the lowest total REE are more strongly humped (Figure 9 lower) than those with higher total REE (Figure 9 upper), which are closer to unity and markedly flatter. This pattern suggests the mixing of two REE sources, possibly the coke and the hearth lining.

Sample details

YSF2 (Figure 10a-h; Plates C3-C5)

This sample is from the highly irregular margin of a slag cake. Up to 80mm from the margin, the upper vesicular section of the slag reaches the base, producing a rather chaotic texture in which the slag has large vesicles and large re-entrants from the base. These cavities may be lined with small debris of slag fragments and fuel fragments. At about 120mm from the margin the slag has thickened to 50mm and assumes a more conventional appear, with a

central dense slag with tubular vesicles, overlying a thin irregularly and finely vesicular basal section and overlain by a 20mm of coarsely vesicular slag (with an irregular, slightly lobate, top).

The primary phase is comprised of sparse, stubby, wustite dendrites, up to 200µm across. These are followed by complex phosphoran olivine, probably with individual crystals many millimetres across, but subdivided into smaller blocky, equant components, approximately 300µm across. Complex zoned spinels are abundant, often occurring in alignments or zones which pick out the larger scale structure of the olivine. Rounded vesicles of up to 400µm are abundant. The vesicles provide a focus for late alteration of the primary minerals, but do not appear to be associated with any variation in the primary assemblage. The interstitial areas have dominant laths/plates of phosphate mineral 'A'. End-member phosphoran fayalite overgrowths enclose small inclusions of graffonite(?). Within the interstitial areas the wustite is strongly overgrown by phosphoran iscorite.

YSF3 (Figure 11a-b; Plate C6)

This sample is a fragment from a slag flow with a finely dimpled base, with many dimples containing small (<5mm) clasts of coke and coal. The lower few millimetres of the slag also contains a few small coke inclusions and small vesicles. The lower section of the slag flow (up to 37-45mm from the base, is marked by very elongate olivine crystals, apparently up to 35mm long. There are sporadic tubular vesicles up to 3mm in diameter through this zone. The slag is dense with a metallic to iridescent appearance. The upper part of the slag follows a marked and abrupt change to a highly vesicular layer, up to 30mm thick, with vesicles of up to approximately 15mm. The top of the specimen is formed by intersecting smooth concave surfaces at least 80mm across, probably indicating former very large tabular vesicles, now unroofed.

The primary phase is of mainly rather stubby wustite dendrites up to 300µm across. The subsequent phosphoran olivine is of complex morphology, with large crystals formed of small units of varying size (50-500µm). The olivine also shows very variable relationships with other minerals – locally forming an early cotectic with wustite, locally a later cotectic with hercynitic spinels, and in a few crystals showing both relationships successively. Complex zoned spinels also occur in a euhedral or subhedral form, locally nucleating on the wustite dendrites and sometimes up to 100µm across. The interstitial areas are variable, in some cases having the typical laminated microstructure, but in others the phosphate mineral 'A' forms a simple pore-filling phase.

YSF4 (Figure 11c-h; Plates C7-C9)

Primary wustite forms small dendrites up to approximately 200µm across. Phosphoran olivine commonly shows a fine cotectic relationship with wustite in its core. The outer parts of the phosphoran olivine are either simple, or, rarely, show a cotectic relationship with hercynite. The outer part of the olivine commonly overgrow more euhedral, complexly-zoned hercynite, which may show a distribution more associated with the nearby wustite dendrites than the olivine. The interstitial areas have a strongly foliated microstructure dominated by phosphate mineral 'A'. The interstitial iscorite overgrowths on wustite are commonly themselves overgrown by small blebs of iron sulphide. The interstitial areas commonly show some residual porosity which is partially occluded by a late-stage hydrated phosphate.

YSF5 (Figure 5c; Plate C10)

This piece has a slightly flow lobed top, but is internally highly vesicular. It thickens from 40-70mm inwards over 200mm. The basal 20mm shows a hint of preferred upward orientation of the vesicles, but the remainder is chaotic with vesicles to 60mm wide.

The gross structure shows the flat top of the specimen overlying a slag with large and abundant vesicles, any of which are vertically elongate, if not fully tubular. The slag shows a rather variable primary wustite; locally with well-developed dendrites up to at least 600µm across, in other places a more irregularly blebby or granular texture. The wustite is abundant where it occurs, but a lack of primary wustite marks the location of many further, but now occluded, vertically oriented vesicles. In some of these cavities the phosphoran fayalite forms fine branching dendrites that do not fill the entire pore. In some pores there are both elongate and botryoidal growths of late hydrated phosphate minerals. For most of the slag the phosphoran olivine has a more typical texture and bears cotectic hercynite locally.

YSF8 (Figure 13f-h; Plates C14-C15)

This sample is a lenticular fragment of slag. The interior is highly vesicular, but crudely foliated, picking out a lower, slightly less vesicular section, 20mm thick, and an upper, highly vesicular section, with a lobate top over very large vesicles. The top is only preserved where the slag is thin – as it thickens the very open textured slag has fragmented and the top is lost. The planar top near the margin suggests the piece would have thickened from 25mm to 60mm over 150mm.

This sample presents a rather different typical texture, or range of textures, to the other refining slags. Much of the slag shows a degree of alteration from its primary microstructure, possibly because of the effects of circulating steam after solidification.

The base of the slag is highly altered and difficult to interpret, but appears to contain clasts of fuel, and possibly of corroded iron, in an iscorite-rich slag matrix.

The lower part of the slag shows a somewhat 'annealed' appearance, with a coarse texture of mildly phosphoran olivine, large plates of iscorite and phosphate mineral 'A'. In places the phosphate mineral 'A' bears laminae of an iron calcium phosphate. The large olivine grains bear crystallographically oriented porosity.

The upper part of the slag shows some areas of relatively 'normal' texture for the refinery slags, interspersed with area of intense alteration associated with vertically extended vesicles. These zones of alteration appear to represent 'chimneys' of alteration. These zones of alteration have been largely described above, under the 'mineralogy' section.

YSF9 (Figure 12a; Plate C16)

This piece was from a highly vesicular sheet-like fragment of slag. The base is granular, with much adhering fragmented slag. The base is highly irregular. The top is crudely flow-lobed, and is again highly irregular. The interior is strongly vesicular throughout.

This highly vesicular sample shows primary wustite dendrites of up to 500µm across. These are volumetrically important over much of the specimen, usually form well-developed dendritic arrays, but are absent from areas of presumed early porosity (now almost entirely occluded by the main phosphoran olivine dominated slag). The final areas remaining as open porosity sometimes show unusual

surround slag compositions and textures. This includes zones with iron calcium phosphate bearing skeletal ghosts of highly phosphoran olivine (0.48 and 0.59 APFU phosphorus) and dendritic growths of magnetite and iron sulphides.

The slag is unusual amongst the refining slags for possessing iron oxide-rich chilled flow lobe margins (resembling those of a tapped bloomery slag). Much of the slag is relatively rich in iron oxides – not just the primary wustite dendrites (with abundant magnetite), but also large plates of iscorite. As with other samples the slag is rich in complexly zoned highly substituted hercynite, which is often enveloped in the outer portions of the phosphoran olivine.

YSF10 (Plate C17-C18)

This specimen is a tabular to very slightly wedge-shaped fragment of slag up to 32mm in thickness. The base of the slag is finely dimpled and rather irregular in shape. The dimples may contain small (<5mm) rounded pieces of coal and coke, with similar materials occur as clasts within the basal few millimetres of slag (which may also be finely vesicular). Above the basal zone, the slag is dense with sparse tubular vesicles (of up to 2mm diameter), but this is locally replaced by more vesicular material. Typically the vesicular material overlies the dense slag, and is up to 20mm thick. The top is smooth and flat, locally with concave depressions that may be large unroofed vesicles.

The primary phase is wustite, with a very low density of small stubby dendrites up to 200µm in length. This sample shows a clear large-scale structure to its phosphoran olivine, with individual crystals being up to over 8mm in length. The olivine frequently encloses the complex zoned hercynitic spinels, which are also seen in the interstitial areas. Where the wustite is exposed in the interstitial areas it is overgrown by iscorite, which is in turn locally overlain by small iron sulphide blebs. The main interstitial phase are foliated crystals of phosphate mineral 'A', between which are phosphatic materials of lower alkali content bearing delicate dendrites of iron sulphides..

YSF25 (Figure 12b; Plates C48, C49)

This sample is a fragment of a wedge-profiled (18-33mm) slag cake with a lightly raised margin, possibly over a particularly vesicular patch). The base is very dense, partially smooth and dimpled, elsewhere, finely granular and porous but very hard. The main body of the slag is dense, with very little vesicularity, although there are tabular vesicles 5-9mm below the top in places. The top is a planar, smooth flow surface. This slag specimen is from a flat-topped sheet that must have been very fluid.

The SEM sample shows a progression from a wustite-poor slag with many large vesicles (up to several millimetres diameter, usually rounded, although sometimes with margins of faceted phosphoran olivine), down to a slag with a low, but persistent amount of wustite.

The primary wustite is in the form of short stubby dendrites, rarely as much as 200µm in length. They are irregularly distributed, with gaps in the distributions, demarking early vesicles, where they are absent. The centres of many of these wustite-free patches still retain a low proportion of porosity.

The phosphoran olivine mainly shows compositions of 0.06 to 0.08 APFU phosphorus, but crystal margins show values as high as 0.56 APFU phosphorus. The zoned spinels are present both within the olivine and in the interstitial areas. It is significant that examples well within the olivine do not tend to include the outer Al-rich hercynite seen in those in, or close to the interstices of the olivine. Interstitial areas are

filled by foliated phosphate mineral 'A', interlaminated with a slight less alkali rich material in a cotectic with minor sulphide threads. Compared to other samples YSF25 has a reduced proportion of phosphoran iscorite.

YSF26 (chemical analysis only)

This specimen is an extremely dense slag sheet, with a very smooth planar upper surface, just slightly rising around the margin on one edge, and locally (although abraded) over coarsely vesicular patches in the slag below. The base is dimpled and locally has a smooth surfaced frothy veneer extending in a thin superficial sheet. This may possibly be the result of contact with water. The internal slag is very dense in places (17-32mm thick), but with tubular vesicles in others (possibly corresponding to areas with a rough base. The tubular vesicles terminate in a local horizon of tabular vesicles 3-7mm below the upper surface.

YSF27 (Figure 12c-e, Figure 13a-e; Plates C50, C51)

This is an unusually dense slag. It has a plano-convex profile, up to 35mm thick in the centre decreasing to 25mm on the edges of the fragment. The base is hard, smooth and slightly dimpled. The internal texture is mainly very dense, there are very rare tubular vesicles and tabular vesicles with partial coarse crystalline margins in the upper section. The slag appears finely granular, and lacks the bladed texture of other samples. The top is apparently a rough, granular crust, possibly with the crust more wrinkled by contraction than flow.

This sample shows an interesting degree of alteration to its base, which is described above under 'mineralogy'. It is the magnetite crusts on this surface which give the base of the specimen its hard smooth appearance.

The primary phase is stubby growths of wustite, typically less than 100µm in length and strongly overgrown by iscorite and closely associated with the hercynitic spinels. The main slag texture of this piece is particularly rich in spinel, which lies in zones and clusters. The phosphoran olivine commonly shows development of a cotectic with wustite in its core, but the cotectic occupies a low proportion of the overall grain. The phosphoran olivine overgrows the spinels in many cases – and where they are deep within the olivine they lack the extended outer hercynite zones. The interstices are, as typical, filled by foliated phosphate mineral 'A', interlayered with material of a similar, but less alkali rich composition, intergrown with iron sulphides. Other phosphate minerals, including the possible graffonite, and phosphate mineral 'B', also occur in the interstitial areas and intergrown with the outermost layers of the phosphoran olivine. The most phosphorus-rich phosphoran olivine present in and around the interstices of the main generation of olivine is amongst those with the highest degrees of substitution identified in this project.

YSF28 (chemical analysis only)

This sample has an unusual morphology, being a concavo-convex slag sheet, up to a maximum of 18mm thick in the flat central part and 10mm on the upturned edges. The slag has a dimpled base with very small fuel clasts (<5mm) and attached slightly larger ones of slag (up to 15mm). The lower surface is smooth and finely dimpled where not covered in attached slag debris. The upper surface is smooth and interrupted only by the open upper ends of some of the tubular vesicles present in the slag (up to 4mm diameter). The slag itself is cut by the tubular vesicles, with a slight row of more tabular vesicles just below the top in the thicker areas.

YSF29 (Figure 12f-h; Plates C52,C53)

YSF29 shows abundant evidence for late (post-depositional) alteration and weathering. The specimen is from a thin slag bowl, ranging from 7mm thick on one edge of the piece to 20mm lower down. The base is smooth and finely dimpled, the slag is entirely vesicular, and the top is obscured by accretion, but appears rather irregular.

This sample shows well-developed initial dendrites of wustite (locally as much as 1mm across), that have become very heavily altered to magnetite and overgrown by iscorite. The subsequent phosphoran olivine shows a wide range of composition. The olivine shows a probable cotectic with hercynite, for the enclosed hercynite is dominantly anhedral. Some euhedral/subhedral zoned spinels occur in the interstitial areas. In general spinels are less significant in this sample than others. The interstitial areas show the usual textures, dominated by the foliated phosphate mineral 'A'. Late sulphide appear less in this samples than in others, however.

YSF32 (chemical analysis only)

This sample was a large wedge-sectioned block, 200mm across, thickening from 50 to 80mm. The base is rough with adhering materials, and is planar. The lower part of the slag forms a sheet of massive slag, with elongate crystals and an iridescent sheen, approximately 30mm thick. The upper layer is highly vesicular and thickens from 10 to 40mm across the piece. The top is approximately planar, with a series of large unroofed tabular vesicles.

Discussion

The refinery slags present a coherent group of materials, with a limited range of chemical and mineralogical composition. The gross structure of the slag cakes appears to be controlled by the loss of volatiles – probably including both the intrinsic materials of the slag and water vapour from cooling in an extremely wet environment. Variation in the interaction with water may also explain some of the larger variations seen particularly with YSF5, from within a drain, but also the two samples showing hydrothermal alteration – YSF8 and YSF27. Although the upper surfaces of many examples show flow lobes, only YSF9 showed internal evidence for chilled lobe margins; it is likely that both the rapid nature of the flow and the subsequent internal homogenisation by movement of the volatiles have destroyed any primary internal flow structures in the other examples.

This assemblage provides the first modern direct evidence for the chemical composition of refinery slags. They have been shown to have a surprising ability to have absorbed phosphorus – and also to have incorporated it within metastable phosphoran varieties of the typical slag minerals olivine and iscorite.

Truran (1863, p.197) gave figures for the throughput of a refinery, stating that 1 ton of refined metal was produced from 23.3cwt of normal pig, producing 3 cwt of 'cinder'. He used analyses to suggest that the silicon in the iron was reduced from about 3.7-4.5% to 0.5%. The analyses of pig iron from Ynysfach quoted above do not suggest such a high initial silicon content, but it is not clear if any of the iron analysed in this project would be typical refinery feedstock.

It is not possible to create a proper mass balance description of the reaction for many reasons, including non-closure of the system (gas, airborne particulates, material carried off by the quenching water...), the unknown role of the hearth lining (likely to have contributed significant silica to the reaction) and the unknown composition of both raw pig and finers metal.

However, the analyses indicate that not only silicon, but also manganese and phosphorus must have been removed from the pig in large proportions.

2.e. Description of materials: refinery micro-residues

General

Despite the contemporary references to these spheroids, their abundance, particularly in the drains, was an unexpected characteristic of the site.

Percy (1864, p.624) mentioned the production of spheroidal micro-residues:

'At the Blaina Iron-works, the twyers were inclined than I have seen elsewhere in South Wales. It was in these refineries that I remarked the formation and projection of minute spherical shots. I saw none of these at Cyfarthfa. The inclination should be greater in the case of grey pig-iron.'

Truran (1863, p. 238) also noted their presence:

'The direct loss or waste of metal in the fining process is not great. The 22.3cwts of crude iron produce 1 ton of metal, and on an average 3cwts of cinder, containing from 56-60 per cent of iron. Hence, of the consumption of 22.3 cwts of iron 21.8 are obtained in plate metal and cinder, showing a loss of but 57lbs. per ton. This would be still further reduced if the whole of the cinder could be collected, but a portion is carried up the chimney before the ascending blast in the form of small hollow globules.'

The microresidues (Figure 16) fall in two distinct types:

- 1 - spheroids with a diameter of less than 40µm, mainly solid, although a few have a central cavity, formed of dense iron oxides (or very rarely metallic iron).
- 2.- spheroids with a diameter of 100-2500µm, with a large central cavity with a multi-cusped outline and a thin shell (<100 µm), formed magnetite dendrites in glass or micro-crystalline groundmass.

The larger particles are consistent with various contemporary accounts describing the emission of shot-like particles from the refinery furnace, as results of the strong air blast disturbing both the molten iron and the overlying slag. The smaller particles presumably have a similar origin, but from the effect of the air blast on the molten iron.

The samples YSF11 and YSF12 were prepared by wet sieving sediment from drains at 100µm. YSF11a was prepared from <100 µm fraction of YSF11.

Chemical composition

The composition of the smaller, type 1, particles is mostly greater than 88% iron oxide (Figure 17a-17b; Table 14). The ratio of iron to oxygen indicates that the iron varies from average combinations equivalent to magnetite, through to very oxygen-rich combinations indicative of hydrated phases. The iron oxide may contain up to 0.2wt% of each of aluminium, silicon and phosphorus, with rare particles showing up to 0.6wt% sulphur. None of the small iron-oxide particles showed detectable titanium, vanadium or chromium.

The bulk composition of the larger, type 2, particles (Figure 17c-h, Figure 18a-h; Tables 13, 15) is close to, but not quite identical with that of the macroscopic refining slags (Figure 15). They share a similar range of silica:alumina ratios. They differ in the spheroids possessing slightly lower phosphorus contents than the macroscopic slags. The REE profile for the bulk samples of spheroidal microresidues (YSF11 and YSF12) are parallel to those of the refining macroresidues (Figure 14). Total REE and the U:Th ratio are within the range of the refining slags. The concentrations of vanadium, chromium, titanium, manganese, sulphur and phosphorus are all slightly lower in

the micro- than in the macro-residues. Although other diluting factors may be invoked, the most likely interpretation of this is that the spheroids are, on average, less evolved than the macroscopic slags, since they have been ejected during the course of the process, rather than at its conclusion.

Mineralogy

The small, iron-rich, type 1 spheroids include some examples where the dominant mineralogy is close to end-member wustite and magnetite (usually with a granular or dendritic texture), with one example being metallic iron with 0.32% phosphorus (YSF SOI31 #3; which has a magnetite overgrowth). The more oxygen-rich particles are interpreted as being of hydrated iron oxides (typically with no observable microstructure), possibly from rusting of metal particles in the depositional environment.

The larger type 2 spheroids, with a lower iron content, are remarkably similar in their microstructure. They show an outer crust of rather coarse magnetite, from which dendrites grow inwards. Most of the thickness of the shell is taken up by a microstructure of these magnetite dendrites in a more-or-less crystalline matrix. Even where the matrix appears (at least at the scale of observation on the SEM) to be a glass, the magnetite dendrites are in some instances fringed with a variegated line of blebs of high and low electron density. In some examples this texture expands into much of the interstitial area, and forms an oriented intergrowth of an iron oxide, probably with silica (although the phases are too fine for meaningful microanalysis). This texture is very similar to the (hydrothermal?) alteration texture of phosphoran fayalite as described above for samples YSF8 and YSF27. A simple dendrite + glass microstructure is only seen in approximately 25% of these particles; in 75% of particles there is some degree of either fringing by, or wholesale development of, the silica-iron oxide cotectic. Only one spheroid (S2; YSF11 SOI4-5) shows convincing indications of survival of crystalline phosphoran fayalite; others may contain phosphoran fayalite, but the bulk composition of the matrix is close to that of the mineral certain identification of fine crystallites by microanalysis is not practical.

These unusual textures are not seen in normal spheroidal hammerscale (Young 2011) and may reflect both the metastability of phosphoran fayalite, and possibly a prolonged period at elevated temperature immediately after initial formation (perhaps in the turbulent hot gasses above the hearth).

One spheroid (particle S41; YSF12 SOI25#2) showed an unusual additional external layer, coating just a part of the outside of the spheroid, which had a very finely crystalline microstructure including dendrites of an iron sulphide.

Sample details

YSF11 (Figure 17e-h, Figure 18a-d)

This sample contained 23 examined spheroids and two other particles that were also investigated. The spheroids showed a low range of variability, as described in the sections above.

The general properties of the spheroids were as described above. Exceptions include S2, which showed a slightly coarser-grained microstructure, allowing zoning in the magnetite dendrites (with cores of up to 4.9% vanadium and 6.1% chromium) and the incipient development of phosphoran fayalite (as wispy dendrites).

For the non-spheroidal particles, P1 was a fragment of corroded grey cast iron, P2 was a laminated ferricreted fine sediment, bearing abundant small type 1 spheroids, of which the composition of 43 examples was measured.

YSF11a (Figure 17a-b)

Following the identification of the small, type 1, particles in P2 of YSF11, a further mount was made (as YSF11a) of particles that had passed the 100µm sieve during the cleaning of the sample for YSF11. A further 24 type 1 particles were analysed. These loose examples closely resemble those present inside the concretionary material of P2, YSF11.

YSF12 (Figure 18e-h)

This sample permitted the analysis of 20 type 2 spheroidal particles. A concretionary particle, P4, contained additional type 1 particles, of which 7 were analysed.

Discussion

Although superficially similar to spheroidal hammerscale (Young 2011), the type two particles show sufficient differentiating characteristics to permit their recognition as a distinct class of micro-residues.

The two classes of particle are interpreted as representing the effect of the air blast on the molten iron (type 1) and molten slag (type 2). The type 2 particles show a composition that is less evolved than the accompanying macroscopic slags – likely to be the result of the ejection of the particles from the furnace during the process, rather than at its end. Nonetheless, the type 2 particles contain sufficient phosphorus to produce an unusual mineralogy and microstructure, that is too fine to resolve fully, but which is suggestive of the development of transient metastability during the quenching of the particles.

2.f. Description of materials: possible puddling slags?

General

One sample of dense slag (YSF30-31) shows a variety of features at macroscopic, microscopic and chemical levels that differentiate it from the otherwise broadly similar refining slags. These characteristics suggest that the slag was produced during the process of dry puddling.

At a macroscopic level, the key characteristics of this piece are that it shows a non-wetted, chilled margin at its base and an adjacent sub-vertical (just slightly splayed outwards) side. The basal surface is mainly planar and suggestive of chilling with a non-wetted contact. Near the margin the main surface is slightly overlain by (or preceded by?) a thin lobe, just 1mm thick, extending in up to about 30mm from the side. The angle to the side is irregularly curved, almost slightly faceted. The sub-vertical side shows horizontal flow lobes, with non-wetted lateral contacts, each lobe 5-10mm high, giving a horizontal striation to the vertical side. The highest point of the slag near the margin is 62mm above the base.

Both chilled margins preserve features suggestive of accumulation from flow lobes, although these have mainly homogenised internally, except, for the basal 10mm which preserves relict flow lobes, some with surviving open horizontal cavities. The main body of the slag is coarse grained, with vertical tubular vesicles up to 6mm in diameter, and is approximately 30mm thick. The tubular vesicles appear to originate from the top of the flow-lobed layer, rather than the base of the cake. The upper 10-15mm of the thickness is variably vesicular and probably passed upwards into a slag rich in large (up to 60mm wide) rounded tabular vesicles, now preserved, unroofed, as the top of the sample.

The lower part of the main body of the slag shows the development of elongate olivine crystals, but these are most clearly seen adjacent to the side wall, where a zone of horizontally elongate crystals (up to 13mm long) marks the zone of slag chilled from the side.

The specimen is therefore strongly suggestive of chilling against the base and side of a metal trough (in contrast to the materials identified as refining slags which show a chilled base on a shallowly-dished surface in most cases). Apart from this the overall structure of the slag and its appearance in hand specimen is equivalent to the refining slags, but thicker.

The sample was divided into two, with YSF30 derived from the low coarse, chilled section and YSF31 from the upper chilled section adjacent to the vertical wall.

Chemical composition

The bulk chemical composition of this specimen shows some similarity with the refining slags, with similar iron content (65.7 and 66.5wt% expressed as FeO; the iron-rich end of the variation shown by the refining slags) and elevated phosphorus (4.12wt% expressed as P₂O₅; slightly lower than that of the refining slags, which have a range of 4.71-6.87 wt% P₂O₅, if the possibly slightly leached slag block, YSF5, that formed inside the drain is excluded). Manganese is present at a level comparable to that in the refining slags (2.63-2.64 wt% expressed as MnO). Silicon is present around the upper limit of the variation seen in the refining slags. Many other elements (Al, Mg, Ca, Na, K amongst the major elements) are at concentrations below the range exhibited by the refining slags. Sulphur is somewhat elevated compared to the refining slags (Figure 15).

The upper crust-normalised REE profiles (Figure 19) for both samples are rather flat, with elevated europium. REE concentrations in YSF30 are approximately three times those of YSF31, presumably due to segregation of the remaining incompatible melt into the lower part of the section of the slag.

Mineralogy

The mineralogy of the puddling slag is similar to that of the refining slags, but with minor variations in mineral composition and proportion, reflecting the differences in bulk composition.

The reduction in proportion of so many of the major elements manifests itself as a reduction in the proportion of the interstitial matrix in these samples; many of the interstitial areas remain as open voids. The other key difference with the refining slags is the abundance of iron sulphides in the interstitial regions, typically forming on or with the phosphoran iscorite.

The paragenesis includes a sparse, blebby early wustite. This wustite shows slightly ambiguous relationships to hercynite in some areas, possibly indicating the wustite was preceded by the spinel. The volumetrically dominant phase is a fayalite-wustite cotectic (Figure 20a,b,c,f,g,h). The outer part of the olivine, beyond the wustite, may envelope complex euhedral hercynite grains and on the margins may partially enclose the tips of large phosphoran iscorite sheets (Figure 20b,c,e). The olivine composition can be modelled as a fayalite with up to 1% calcium and 9-10% manganese substitution. Upon this is superimposed the phosphoran substitution, so that olivine is entirely phosphoran, with 0.05 to 0.08 APFU phosphorus, increasing outwards across the olivine-wustite cotectic. From the edge of the cotectic to the margin of the crystal (typically a distance of about 30µm) the phosphorus increases rapidly, so that analyses as near the margin as possible attain approximately 0.50 APFU phosphorus. Where there are prolongations of the olivine into the interstitial space these show increasing phosphorous all the way up, apparently, to about 0.75 APFU (which a little bit higher than the theoretical maximum quoted by Boesenberg & Hewins 2010). In some locations (e.g. YSF30 SOI14 #2) the end-member phosphoran olivine rests abruptly on olivine of a lower phosphorus content and even (e.g. YSF31 SOI 5 and YSF30 SOI5) may form a distinct interstitial phase of elongate crystals of somewhat rhomboidal form (Figure 20c,f).

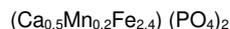
The development of complex hercynitic spinels (figure 20b,e), from chromite- and coulsonite- rich cores to simpler outer regions, parallels their development in the refining slags and has been fully described above.

The presence of the early spinels in the puddling slag does appear particularly controlling on the development of the subsequent phosphoran iscorite. Analyses suggest there is a range of 0.15 to 0.61 APFU phosphorus.

The phosphoran iscorite is followed by a more extensive development of sulphides than in the refining slags. The sulphides may form blebs along the outer surfaces of the iscorite, but may also apparently form within the iscorite and form curious masses with crystallographically-aligned variations in density, in part aligned along the iscorite crystallographic planes, resulting in a cross-section somewhat resembling a pineapple (Figure 20d)). The sulphides are FeS with localised traces of copper and lead.

The late stages of crystallisation involved multiple phosphorus-bearing phases as with the refining slags. Although the relationships are broadly similar, Phosphate mineral 'A' is a less-important member of the assemblage in

most areas of the sample (though present in parts of YSF31), with the iron calcium phosphate the more significant, particularly in sample YSF30. The composition is less calcic than for the graptolite in the refining slags, and it may be that this is a calcium-bearing sarcopside:



Sample details

YSF30 (Figure 20 a-e; Plates C54-C58)

This sample shows a paragenetic sequence as described above. The phosphoran olivine shows string development of a cotectic with wustite (Figure 20b,c), and occurs in elongate crystals with no apparent preferred orientation. Much of the interstitial space between the olivine crystals remains open. Phosphoran iscorite, often with a clear zoning in phosphorus content, is a more significant component of the mineralogy than in other samples (Figure 20c). It forms isolated plates, plates with complex crystallographic interrelationships (Figure 20e) as well as overgrowing primary wustite (Figure 20e)

The phosphoran iscorite is the substrate for nucleation of iron sulphides, frequently forming 'pineapple' like intergrowths of sulphides and iscorite (Figure 20d). The final pore-filling phase is a late hydrated phosphate mineral.

YSF31 (Figure 20 f-h; Plate C59)

This sample shows the zone of strongly elongated, parallel, phosphoran olivine. This has cores of a cotectic with wustite (Figure 20f-h). There is little of no primary wustite in the main texture, but the elongate texture can be seen to be rooted in a layer with wustite (lower part of Figure 20f), albeit with the wustite heavily overgrown with phosphoran iscorite. Most aspects of the texture otherwise resemble that of the lower part of the slag cake (YSF30). In some areas (Figure 20f) substantial open voids exist between the elongate olivine crystals.

Within the zone of elongate, parallel olivine, iscorite is largely in the form of plates aligned along the interstitial zones (Figures 20g,h). The iron sulphide nucleating on the iscorite shows some of the small 'pineapple' growths, but hemispherical masses on the surface of the iscorite plates are also present.

Discussion

The identification of this piece as a residue from puddling is largely based on its chemical composition – which suggests that the slag has not incorporated significant amounts of fuel ash (resulting in a high silica:alumina ratio and low levels of many elements derived from the fuel) compatible with an origin in a reverberatory furnace rather than in the fuel bed of a refinery furnace. The elevated sulphur content of this piece compared with the refining slags is also suggestive of a different process. The evidence for a different environment of cooling for this piece – by chilling against a metal surface – is rather more ambiguous; it could be argued that cooling of the slag within the run-out trough would be consistent with this evidence.

Although each of these three strands of evidence could be explained by different operation of the refinery furnace, their co-occurrence in this one piece suggests that an alternative interpretation should be sought.

Three broad categories of puddling were employed in the 19th century, but all have poorly known residues. As with so many 19th century technologies, the true path of the

development of puddling remains obscure – illuminated only by a few patents and retrospective accounts by old men. Much of the development probably took place within individual ironworks as the result of the skill of the puddlers themselves and remained unrecorded.

The earliest form, dry puddling was that proposed by Henry Cort (patented in 1784) and entailed the use of a sand bed in the reverberatory puddling furnace. The sand bed was attacked by the iron-rich slag that formed on the iron, so the slag would be tapped frequently to reduce the damage. It has been argued that this frequent removal of slag reduced the capacity of the puddling furnace for slag-iron interaction and therefore its ability to refine fully the iron charge.

A variation to the puddling furnace was subsequently developed (claimed by Rogers 1858 to have been a result of his work c. 1816, but also apparently used by David Mushet from c.1815) involved the twin developments of utilising an iron furnace bottom and fettling the furnace with scale or red iron ore. This revised process permitted improved iron-slag interaction in a slag bath and, became known as 'wet puddling' (as opposed to Cort's original 'dry puddling' technique).

Further developments added additional sources of oxygen into the furnace, with the result that a vigorous chemical reaction could be produced, giving the impression that the slag bath was boiling. This invention of the process of 'pig boiling' is usually attributed to Joseph Hall, a puddler at Tipton, in about 1826. Additional oxygen was supplied by fettling the furnace with slag (Hall also patented his preparation of puddling slag by roasting to produce 'bulldog' in 1839) and by introducing scrap iron into the charge. In most areas, 'pig-boiling' was sufficiently effective at oxidising the impurities in raw pig iron, that the refinery process became redundant.

Very few examples of puddling slag have been described in the modern literature. Killick & Gordon (1987) published material collected at Cort's Fontley works and interpreted as representative of 'dry puddling'. Their analysis shows the Fontley slag to be very siliceous ($\text{SiO}_2 = 36\text{wt}\%$, $\text{Al}_2\text{O}_3 = 0.5\text{wt}\%$) and they deemed the presence of silica grains to be characteristic. This certainly seems quite distinct from the present material. Analyses quoted by Percy (1864) for residues from later variants of the process include a broad compositional range, including material of similar compositions to the present material.

At present, this material may only be assigned to the puddling process with some doubt. It is possible it represents a residue from refining outside the range of compositions of the other residues examined. However, to differ from the identified refining slags on several aspects of chemical composition as well overall texture, seems likely to suggest a different origin.

2.g. Description of materials: Bessemer converter tuyères

General

The site produced three examples of siliceous ceramic tuyères from Bessemer converters. The three examples were all incomplete and had been used. They were all constructed to the same design, with a ring of eight bores, surrounding a single central one, each of 0.5 inch (12.5mm) diameter. They were, therefore, similar to the original implementation of Bessemer himself in the 1860s, but with 9, rather than 7, bores.

Sample Details (Figure 21)

A tuyère fragment from context (194) (Figure 21) is split across its diameter, as well as across its width 160mm above the base. The base is approximately 180mm in diameter. The lower 40mm has a simple inward taper, down to a diameter of approximately 160mm. There are surviving parts of nine perforations (3 complete and 2 half examples of an outer ring of 8 (85-90mm diameter), plus one centrally). Each perforation is slightly irregular, but appears to have produced to an intended ½ inch diameter (12.5mm). On the lower face some holes show a very slight lip of deformed clay around the perforation. The fabric comprises rounded silica grit in particles of up to 3mm, set in a pale paste, the whole having a slightly off-white cream colour. The piece shows two adhering blebs of pale translucent brown glassy slag on the basal surface. Five of the perforations are occluded by rusty iron slag.

A second example (from context 126; now in the NMW Collections) is also of the basal section of a tuyère. This is preserved for 265mm above its base, which is 185mm in diameter. It shares the same profile as the specimen above, narrowing to approximately 150mm at the most distal preserved section.

A third example (from context 126) is from the distal end of tuyère, with an eroded and slagged tip. The tip is approximately 150mm in diameter. It bears up to 15mm of slagged material, with an irregular surface indicating preferential erosion around the outer surface of the tuyère, as well as in localised areas around some of the perforations. All the preserved perforations are open. They are approximately ½ inch diameter (12.5mm), and as with the previously described example, there would have been 8 in a ring and one central. The fabric is similar to that of the previous example, but grits of up to 6mm are visible. The fabric shows evidence for cracking towards the tip, with slight irregular cracks showing discoloration.

Discussion

The tuyères are very similar, but not quite identical to the assemblage of ten tuyères recently recovered from excavations at the Cyfarthfa Ironworks coking plant. The differences are in the form of the perforations: those from Cyfarthfa have a basal section which widens to 5/8 of an inch (17mm) diameter, to form a wider air inlet. The impression left by the forming equipment also commonly forms a depressed ring or funnel-shaped depression around each perforation, typically of 1 inch (25mm) diameter. In one tuyère from Cyfarthfa, of slightly different shape the distal bore was as low as ¼ inch (6mm) with a 30mm diameter tool impression around.

Despite the subtle differences, the tuyères from both sites had the same overall shape, size and bore location. There

is no reason to suppose the two assemblages of tuyères could not have been used on the same converters.

The development of the Bessemer converter is not well documented. One of the early alterations to Bessemer's original design was to increase the airflow. Almost all descriptions and illustrations of tuyères from the 1860s show seven holes (e.g. Bessemer 1905, Plate XV; Percy 1864, p.823).

Developments during the 1870s and 1880s can be followed by the detailed descriptions provided by Howe (1890), notwithstanding the American slant to the coverage. Tables 196-198 of Howe (1890) provide summaries of numbers of tuyères, perforations and tonnages for the period. Most works of the period appear to have approximately 1 to 6 square inches of perforation per ton of capacity. He stated that a typical 15 ton converter would have had 250 ½ inch holes.

Stoughton (1908) quotes Howe's earlier work, but also adds that 3/8 inch diameter holes were typical in England, whereas American works employed holes of between 3/8 and 5/8 inch.

Macfarlane (1917) quoted (p. 66) that in '*one works the 18-ton converters each have 24 tuyères, and that each tuyère has 19 holes of 5/16 inch diameter. This equals 35 square inches of tuyère hole area, and may be accepted as fairly representing British Bessemer (acid) practice in this particular.*'

For the present material, each tuyère has 9 perforations, each of 0.5 inch diameter. This gives a total of 1.77 square inches total perforation per tuyère. The ratio quoted by Macfarlane would suggest that the 8 ton converters at Cyfarthfa (Ince 1993, p 64) might have employed 8 tuyères. The earlier ratios presented by Howes (1890) would suggest that the total area of hole might be between 8 and 48 square inches (using the whole spread of American and English data), which implies the use of between 5 and 27 tuyères; alternatively, employing the English figures only (i.e. 2 to 3 square inches per ton) would imply the converters would have required between 9 and 13 tuyères each.

These figures confirm that the relatively large bore of the tuyères from Ynysfach would be provide sufficient air to be compatible with a rather simple converter of 8 tons. A small number of these tuyères would be needed. Such a configuration would be entirely in keeping with the likely implementation at Cyfarthfa of a converter design of the late 1870s.

2.h. Description of materials: acid Bessemer slags

General

The specimens both comprise examples from slag flows. One is a large bulbous, probably very viscous, pillow-like flow lobe (YSF7); the other is a more conventional flow with a flow-textured upper surface and a very irregular base (YSF6). They contain a variety of clasts, including siliceous pieces, possibly sandstone fragments or siliceous furnace lining, and, in the flow-textured block, fuel (coke). The pillow-shaped block (YSF7) also contained small prills of metal, but unfortunately none was present in the polished block. These textures greatly resemble those of slags from cupola foundry furnaces (Young 2011). Their chemical composition is, however, closer to that recorded for slags from the acid Bessemer process (e.g. Macfarlane 1917 p. 83; Stoughton 1908, Table XIII). It is possible that the coke in YSF7 has become entrained in the environment into which the slag was tapped, rather than in a furnace.

Mineralogy

These two specimens show a similar mineralogy with relict siliceous material (probably from a high temperature siliceous refractory), neomorphic silica (cristobalite or tridymite). Given the presence of a very siliceous melt generated from a lining fragment in YSF7, the temperature reached by the slag is likely to have been greater than approximately 1590C – and therefore the silica polymorph present, at least originally, would be cristobalite.

The silica is widely present in both samples as a neomorphic phase, which has various rosette and dendritic forms, as well as appearing as a very fine blebs.

The second slag mineral is rather more problematic and the petrographic evidence suggests that the dendritic material observed is actually olivine plus silica after a metastable pyroferroite/pyroxmangite group mineral. Similar minerals have been previously recorded from steelmaking slags (Whiteley & Hallimond 1919); Both the metastable pyroxenoid and the olivine show approximately equal levels of iron and manganese in YSF6 and slightly more iron than manganese in YSF7. Where the slags have been chilled they are either microcrystalline or glassy.

The slags bear droplets of iron with low levels of impurities.

Chemical Composition

The bulk composition (Table 21) for the two samples is very similar, with 37-40% of iron plus manganese oxides, 56-60% silica and about 2% alumina. Other major element oxides are in very low concentrations.

Trace element concentrations are generally though, although vanadium, chromium, and nickel are moderately elevated. The REE are very low (total REE of 14-28ppm), as are uranium and thorium (which a uranium to thorium ratio of 0.36-0.46). The upper crust normalised REE profiles are rather flat and low.

Sample details

YSF6 (Figure 23a-e; Plates C11-C12)

This slag has a very inhomogeneous texture, controlled by complex growths of a silica polymorph (tridymite/cristobalite)

in a variety of dendritic, rosette and annular forms. The distribution of the neomorphic tridymite/cristobalite is controlled, at least in part, by the occurrence of highly-altered siliceous clasts which show much internal cracking.

Reaction of the silica clasts has generated a porosity of mainly rounded vesicles of up to about 250µm. These vesicles have locally developed a rim of neomorphic tridymite/cristobalite, which, if the vesicles later became infilled by slag, produce the unusual annular growth form.

The tridymite/cristobalite is typically surrounded by an area of development of very finely porous dendrites, sometimes with rather denser overgrowths. These structures so finely structured as to present great difficulty in analysis, but they appear to be formed of material with a bulk composition equivalent to a pyroxenoid with almost identical iron and manganese contents:



There is a replacement of silicon by aluminium amounting to approximately 0.04-0.08 APFU.

However, the dendrites appear to have very fine inclusions of silica. Analyses (Table 22) of the denser, angular outermost parts of the dendrites show them not to be a pyroxenoid but an olivine, of similar balance between manganese and iron (i.e. 50% fayalite, 50% tephroite).

This material is therefore interpreted as suggesting initial growth of a metastable pyroxenoid (on the pyroferroite/pyroxmangite boundary, although slightly unusual for that group in containing no calcium), which decomposed to olivine plus silica.

The dendrites locally support tiny elongate crystals with a composition suggesting a titanium-, vanadium- and chromium-rich hercynite.

Further from the main tridymite/cristobalite developments, the later phases are finely crystalline rather than showing well-developed dendritic. They too suggest an intimate association between iron-manganese silicates and silica, but they are too fine to determine whether they are a tridymite/cristobalite plus pyroxenoid assemblage, or tridymite/cristobalite plus olivine.

The slag bore numerous small droplets of iron. Three analysed droplets contained up to 0.4% Mn but no other elements above detection limits, the fourth showed no manganese but about 0.3% each of aluminium and phosphorus.

YSF7 (Figure 23f-h; Plate C13)

Sample YSF7 is similar in most respects to YSF6. The slag includes some partially-melted siliceous clasts. The bulk composition of one clast (YSF SOI3) is approximately 95% silica, the remainder mainly being small quantities of alumina, with manganese and iron present both as oxide and in metal droplets. The glass composition was in the range of 85-90% silica. The lack of substantial iron or manganese involvement in this glass suggests that the melt developed at, or close to, the mullite-cristobalite eutectic, which is at 1587±10C on the SiO₂-Al₂O₃ join. This temperature is compatible with the temperatures reached in an acid Bessemer converter.

Microstructures within the main body of the slag were very similar to those from YSF6, with porous dendrites overlain by a horizon of silica and overgrowth of subhedral olivine, with minor interstitial vanadium- and titanium-bearing hercynite.

The only significant difference between YSF6 and YSF7 is the relative concentration of iron and manganese – which were approximately equal in YSF6 but in YSF7 the iron is very slightly more abundant.

Discussion

These slags match the described chemical composition for acid Bessemer slags, but there is a complete lack of comparative data for the microstructure and mineralogy of early Bessemer slags.

The general morphology of the pillow-like block (YSF7) and the apparent presence of coke clasts (YSF6) are both features that might be interpretable as being indicative of slags from a cupola furnace (compare the cupola slags from the Govan Ironworks in Young 2011b). Although such an origin is conceivable, it is problematic to suggest how a chemical composition matching that of acid Bessemer slags would have been arrived at from the cupolas feeding the converters (which would have been separately handling the iron and spiegeleisen).

On balance, an origin of these slags from the converters themselves appears more likely, perhaps with accidental contamination from coke in the dirty converter shop environment.

2.i Description of materials: clinker

General

The specimen (YSF1) was a rather dull-surfaced clinker with lobes separated by lumps of coke. The sample was chosen as a potential fuel-rich material from within the refinery furnace, that might provide further information on the refinery process.

Mineralogy

The material was dominantly glassy, moderately vesicular and very inhomogeneous (Figure 26a-f; Plate C1-C2).

The surface of the slag bears a thin surface layer, up to approximately 3µm thick, formed by small crystals of aluminous magnetite. Similar crystals, although slightly larger (up to approximately 4µm), and rather more equantly euhedral, occur scattered through the outer 50µm of the glass. Other than this, the only neomorphic slag mineral is one of the alumina-silicate polymorphs, almost certainly sillimanite (Figure 24). The sillimanite occurs in elongate crystals up to 300µm with a square cross section of 1-5µm.

The slag bears large clasts of coke, isolated grains of quartz and carries the ghosted outlines of absorbed clasts.

The glass locally bears abundant blebs of iron, the distribution of which suggests ghosts of clasts in some instances, with particularly strong developments of blebs around the fuel clasts. In most instances this iron shows a measurable level of nickel (up to 3.6wt%) and sometimes lower levels of copper. Some of these blebs are at least partially sulphidised, with one example of a partially sulphidised bleb containing 3.4wt% cobalt, 9.2wt% nickel and 0.5% copper, along with 52.6wt% iron and 17.0wt% sulphur. The distribution of these iron blebs suggests that the cobalt, nickel and copper may be derived from the fuel.

Away from the fuel clasts, the iron blebs tend to lack cobalt, nickel and copper, but instead are more strongly phosphoric – with 2.0-3.6wt% phosphorus.

Chemistry

The bulk composition (Table 23) is rather typical of a clinker: rather aluminous (SiO₂ is 56.0wt%, Al₂O₃ is 23.6wt%, giving a silica:alumina ratio of 2.37), with moderate iron (9.57wt% expressed as FeO), low manganese, calcium, sodium and phosphorus (with 0.19% MnO, 0.23% CaO, 0.33% Na₂O and 0.15% P₂O₅), but with appreciable magnesium (91.83% MgO) and high potassium (25% K₂O). The sulphur content is low (0.088% expressed as SO₃). As would be expected, Y (42.8ppm), Th (16.9ppm) and the REE (total 272ppm) are all high; the U:Th ratio is 0.27. The upper crust-normalised REE profile is fairly flat, but with Sm to Dy slightly and irregularly elevated, and all above unity (Figure 25).

Discussion

The interpretation of this specimen is problematic. The high nickel content of the iron droplets, and the distribution of the droplets around the fuel clasts, suggests that the iron prills may have been reduced from the slag. Nickel occurs in the Merthyr Tydfil area particularly in the mineral millerite, found in cavities in the claystone ironstones (Bevins 1994, 89-90).

The high levels of the nickel (and other normally trace elements) suggest that these droplets have not been homogenised with a bulk iron and, therefore, that despite the presence of iron, that this may not be a slag from iron production.

A more likely interpretation may be, that this is a simple clinker, perhaps from the boilers, that contained sufficient included ironstone within the coal that a small amount of iron-reduction occurred.

3. Interpretation

The archaeometallurgical assemblage from Ynysfach Ironworks produced important new evidence for the nature of the refinery process as practiced in the Crawshay ironworks of the early to mid-19th century. Unexpectedly, the assemblage also included a suite of residues from the steelworks phase of the Cyfarthfa site, with which Ynysfach was not directly involved.

3.a Conversion before refining

The new evidence for the chemical nature of the refinery process provides an opportunity for reflection on why the refinery process was developed. Some consideration of the processes employed before the introduction of the refinery and puddling furnace is therefore required and is given below, with particular reference to the earlier conversion techniques employed at Cyfarthfa.

Accounts of the development of the technology for converting pig iron to wrought iron during the late 18th century have been provided by various authors, including Birch (1967, 30-41) Mott (1983), Hayman (2003) and King (2011). Study of the development of forge technology during the second half of the eighteenth century is hampered by the imprecise and changing meaning of technological terms, together with the rather vague wording typical of patents in the earlier part of the period.

During the first half of the 18th century the adoption of coke for iron smelting was slow. Initially the coke-smelted iron was used almost entirely for castings; charcoal smelted iron, converted in the finery forge with charcoal, remained the main source of bar iron. From 1729 onwards (according to Mott 1983) the Coalbrookdale works produced bar iron from coke smelted iron, by careful selection of low phosphorus ores, but still using charcoal fineries.

During the 1760s a burst of trials and patents demonstrates that the issue of conversion using coal was being tackled by a large number of works independently.

The dominant conversion technique in the second half of the 18th century came to be known as 'potting and stamping'. The technique was covered by two early patents: No. 759 of 18th May 1761 to John Wood and No. 794 of 26th November 1763 to John Wood and Charles Wood. These patents are particularly relevant to the subsequent development of conversion forges in Merthyr Tydfil because in 1766 Charles Wood was taken on by Anthony Bacon to supervise the construction of Cyfarthfa Ironworks. Charles operated the Low Mill forge in Cumbria, where he undertook much of his experimentation. Charles' second wife was the sister of William Brownrigg of Ormathwaite Hall, who was Anthony Bacon's partner in the Cyfarthfa venture. Charles Wood kept a diary during this period (Gross 2001; covering the periods 11th April 1766 to September 1766 and from 11th April 1767 until May of that year, but the diary also includes notes on other periods in the 1750s. Thus the Wood 'potting and stamping' process is documented via the patents and also through the detailed description of the construction of the works to house it (the Cyfarthfa Lower Works).

Wood's process was a complicated one, with four variants described in the 1761 patent (Mott 1983, p3):

1. Pig iron was melted in a common finery, but using raw coal as fuel, until it was brought near to a malleable state, the 'iron thus flourished' was put into closed pots and rendered malleable by reheating in a coal-fired air furnace.
2. The iron was melted in a coal fired air furnace and crushed under water. The granulated iron was then mixed

with fluxes and scale and heated in closed vessels in an air furnace.

3. The cast iron was melted into thin plates, which were then broken and placed in pots for reheating in an air furnace.

4. An adjustment to the process, so that malleable iron was mixed with the stamped iron in the pots if the iron quality was poor.

The 1763 patent mentions the use of a waterwheel powered stamp to crush the iron in case 3.

Wood's diary provides some details about how this was implemented at Cyfarthfa. Much of this is localised detail, often with a lack of clarity, and there is no overall plan of the works given or described. He describes building a 'flourishing house' with a granulating cistern (Gross 2001, 182-183) and flourishing furnaces (whose ash pits and stack are recorded, indicating they were air furnaces), a waterwheel powering two stamps, apparently housed in the same building as the forge, a water powered chafery and at least five shingling furnaces, associated with two water powered hammers, a water powered clay mill (with rolls), with adjacent drying room for the pots and four kilns, and a mixing room, with bins in the wall allowing the granulated metal to be fed from the stamping house.

On 30th August 1766, he pondered the value of a railway to move coal (Gross 2001, p. 137) and in doing so gives some information about the proposed works – namely that the blast furnace would produce 18 tons of iron per week, supplying four flourishing furnaces and two shingling furnaces (all using coal or coke); these figures do not agree with information given in the rest of diary however.

There is much further detail to be teased out of Wood's diary, but it would appear the process used employed air furnaces for 'flourishing' (a term of uncertain meaning, taken as implying desilicisation by Evans, but partial decarburisation by others), followed by water-powered stamping, washing, then packing the granulated metal in pots, which were heated in further air furnaces (the shingling furnaces), before being hammered and the bar iron finished at the chafery. What is unclear is how the flourishing furnace actually worked. Was it simply replacing the use of a 'common finery' in example 1 of the 1761 patent, or was it used to cast plates, as in example 3? One possible clue is mention of the use of an air furnace for casting various components in May 1767. This seems to imply the adapted use of a flourishing furnace, and note is made that '*there was a Stone put where the Tap hole ought to have been*' (Gross 2001, 189; 6th May 1767). This may imply conversion of the air furnace from its original purpose, or that it had been built incorrectly and was intended to have a tap hole. Clearly, the ease of conversion may well imply that the air furnace was built with casting in mind, and therefore it is possible, although far from certain, that example 3 of the 1761 patent, the casting of thin plates, may have been the intention.

In a letter of 3rd March 1791 (Evans 1990, p. 95-96) Richard Crawshay describes his conversion process:

'we make use of Air Furnaces instead of Finerys, when the Metal is bro.^t into nature, instead of Hammers, we put it between a pair of Rolls, & crush it like a paste about ¾ in thick – then we break it into small pieces, pile up 60 to 80 lbs w.^t on a Cake of baked Clay, heat 20 of those piles at a time in a.^t Air Furnace, then shingle them under a Hammer of 1200 lbs w.^t fixed in an Iron helve of 2 tons w.^t The blooms thus finished is again heated in an Air Furnace & bro.^t into a very handsome Bar by Groov'd Rollers... to make 'em straight & handsome, we planish 'em under a lighter Hammer'.

A later description of (apparently) the lower works at Cyfarthfa is quoted by Birch (1967, p. 77-78; based on a visit by Peter Ewart, a Boulton and Watt engineer in 1793) and lists '2 *plishing forges*, 4 *melting fineries* and a *rolling mill with 2 pair rolls*, for *Rolling bars out of ½ blooms turned by a water wheel of about 20 feet diameter*'. Thus, at Cyfarthfa, it is plausible that the melting fineries were air furnaces.

An alternative process was stated by Patent No. 815 of 1766 to Thomas and George Cranage. This claimed to permit conversion of pig iron using first a heating in a reverberatory furnace with a sand bottom, until 'brought to nature', followed by a second heating also in an air furnace. Few details are known and the process does not appear to have been successful.

In 1771 John Cockshutt took Patent No. 988, with a process involving first fining the pig in a coal fired finery and then finishing the process in a charcoal finery. John was the elder brother of James Cockshutt who was Crawshay's manager at Cyfarthfa between 1788 and 1791 – the key period for the development of the refinery. Percy (1864) certainly saw in this patent the idea that was developed into the later refinery:

'I have not yet been able clearly to ascertain the history of the refining process, which, probably was gradually arrived at. In 1771 a patent was granted to John Cockshutt, for "making malleable iron directly from the ore in a finery or bloomery," and "refining pig-iron with charcoal into wrought-iron," and "a new finery or bloomery." The finery is described as made of metal plates, open on two or more sides, so that men might work on at least two sides. Instead of only one twyer, there were several, "so as to direct the wind from the bellows to operate upon the iron in every part of the fire." The number of twyers was to be regulated according to the nature of the iron, There is, obviously, a considerable resemblance in construction between the "new finery" here described and the modern refinery.'

A further patent (No. 1054) was issued to John Wright and Richard Jesson of West Bromwich in 1773, for a variant of the 'potting and stamping' process. This entailed heating cast iron with scale and slag in a normal finery, but using coal or coke. The product was taken out and beaten to plates under a large stamp, and the plates themselves broken by a second stamp. The fragments were then washed and heated in a closed pot in a reverberatory furnace, before shingling with a chafery. A second patent (No. 1396 of 1784) described piling the flattened cakes and reheating them without the use of pots. King (2011) identified the presence of 'melting fineries' in forges built after 1785 and on the c1790 list of forges, as an indicator of the use of Wright & Jesson's process, but it is unclear precisely what a 'melting finery' was.

The final influential patent of the period before that of 'puddling' by Cort in June 1784, was that (No. 1370) taken by Peter Onions in September 1783. Onions developed a process very similar to puddling, but with the addition of an opening to allow the furnace to draw fresh, cold, air onto the iron (Percy 1864, 637-639; Mott 1983, 13-15). His furnace was aided by a blast directed into the firebox, rather than simply relying on the draw of the chimney as in Cort's puddling furnace, but the idea and practice are clearly very similar (despite the protestations of Cort's biographer, Mott). To aid the work of the air furnace, Onions describes introducing the iron pre-melted from a 'common furnace'.

Cort's patents for improved rolling with grooved rollers of 1783 and most importantly his patent for producing wrought iron from cast Naval ballast in a reverberatory furnace (No. 1420, 12th June 1784) were followed by a period in which Cort toured the country with his processes, trying to convince potential licensees. During late 1784 Cort ran

various demonstrations particularly aimed at winning over the ironmasters of the West Midlands, but also of Scotland. These trials were documented in various pieces of correspondence quoted by Mott (1983, p. 47-50) and by Anderson & Jones (2012, p. 704-711, p.787-792, p.866-873, p.883-884). During the early trials with naval scrap at Fontley, Cort had demonstrated his process worked well, but when faced with processing raw pig iron in these trials, the results were more mixed. Some iron was thought to forge well, but increasingly samples of iron produced by Cort's process were not well regarded. The type of defect is exemplified by a letter from William Reynolds to Joseph Black (2nd March 1785; Anderson & Jones 2012, p. 869): *'... the Nailors who have tried the Iron Slit at Bromwich pronounced it to be of good quality for Working as it is soft, and Yeilds very well from the Rod to the Nail – but I must beg leave to say at the same time that the Nails I am afraid will not clinch well as they will break upon being bent & then reversed'*. Amongst the material tried by the nailers was iron fined from 'Mr Homfrays Welch Pig' (Anderson & Jones 2012, p. 869) resulting from the trial in Wednesbury on November 26th, 1784 (Anderson & Jones 2012, p. 790-791).

In fact, James Watt had earlier commented on the quality of Cort's iron (Anderson & Jones 2012, p. 710):

'The kind of iron you describe is known here by the emphatic name of rotten tough/ I have long known that almost any cold short Iron may be brought to [that/ state, by rolling it very hot, or by drawing it across the navil so as to spin the Crystals into threads; & by certain mechanical processes good Iron may be rendered Cold Short, nevertheless in neither of the cases the quality of the Iron is altered The good Iron continues strong and the Cold Short is very weak. I look on Mr. Cort's Iron as a Cold Short whose crystals are spun out by the rolling, and which is mixt with a large quantity of half metalled earth. It is tender to the file and soft to the hammer, rusts very readily, and ought never to be used where it is subjected to any strains as it is very weak, therefore unfit for Engine work Ship work etc. but good for nails, because easily wrought, but there are nailers complain that it wastes more than the com^d cold short, I suppose because not so well freed from its cinder. Good Iron is hard under the hammer & stubborn to the chisel & file, breaks white, generally granulated, but the very best is fibrous & white like silver --- I find I am getting into a dissertation on Iron, which I must shorten.'

These descriptions of Cort's iron do indeed resemble descriptions of iron with an excessive phosphorus content.

Within 3 months of Richard Crawshay taking the lease on the Cyfarthfa works, he had taken a license on Cort's process (1st May 1787). Following trials at Fontley, Cockshutt (Crawshay's manager at Cyfarthfa) proposed building eight new 'Cort's' furnaces on the Boring Mill stream. Both the new process (producing what Crawshay referred to as 'patent blooms') and the old 'potting and stamping' process continued in parallel. Crawshay's letterbook of the period was peppered with complaints about quality (Evans 1990, 4, 6, 7, 14, 16, 25, 29, 30, 35, 40, 41, 42, 49, 54, 71). By September 1790 Crawshay was writing (Evans 1990, p. 77) 'I fear we must give up puddling at last'. On 12th October 1790 (Evans 1990, p. 78), Crawshay instructed Cockshutt to set up two new fineries in the Lower Works to increase the make of stamped metal. However, by 26th November 1790, Crawshay reversed this and told Cockshutt to extend the puddling to the lower works as well, by exchanging the stamps for rolls.

On a list of forges dated 1794, but probably collated in 1790 (King 2011), Cyfarthfa appears as having 2 coke blast furnaces, 3 melting refineries, 3 balling furnaces, 1 rolling mill and 8 Cort's furnaces.

By June 14th 1791 Crawshay was able to give some significant figures for the puddling process: twelve tons of pig iron were consumed in each finery every week. The wastage of iron in making finers metal ranged from 20 to 23 cwt. A finer received 6/- for each ton of prepared metal. An average of 7 tons 5 cwt of finers metal was made up into loops in each furnace weekly (Evans 1990, p. 107). In a letter to Cockshutt on 30th June 1791 (Evans 1990, p. 107) Crawshay advised that 'the performance of the old furnace is so poor it would be better to blow it out and divert its blast to blow more fineries'. These items suggest that the refinery was in use by June 1791, but whether the introduction of the refinery was the cause of Crawshay's change of heart between September and November 1790 is not clear. The letter of March 1791, quoted above (p.22), describing the Cyfarthfa conversion technique, seems to imply that at that date a piling version of 'potting and stamping' was still being used.

After dissolving the Cyfarthfa partnership, Crawshay took direct control of Cyfarthfa and moved to Cyfarthfa House in September 1791; by December of that year he was able to state that he now practiced a new and unique technique at Cyfarthfa (Evans 1990, p. 120) and finally on 29th December 1791 (Evans 1990, p. 123). He was able to tell William Reynolds that he has 'at last overcome the Evils of pudling'.

3.b. The development of the refinery

Contemporary descriptions of the refinery process are of various kinds. Many of the early descriptions are to be found in various technical dictionaries, including Ree's *Cyclopaedia* (1811), *Encyclopaedia Britannica* (1824) and Ure's *Dictionary* (Ure 1839, 1840, 1843; Hunt 1861, 1867). Another rich source of early information are reports on visits to British works by French metallurgists and geologists (Bonnard 1804-5; O'Reilly 1805; Hasenfratz 1812; Dufrénoy & Élie de Beaumont 1827; Coste & Perdonnet 1830; Dufrénoy, Élie de Beaumont, Coste. & Perdonnet 1837). English language technical books and treatises become frequent slightly later (Herbert 1836; Overman 1851, 1852, 1854; Phillips 1854; Truran 1855, 1863; Percy 1864; Bell 1884).

The first detailed published description is that by de Bonnard (1804-5) following his visit to Britain in 1802. O'Reilly republished de Bonnard's account (O'Reilly 1805) with annotations incorporating his own observations on a visit to Britain, probably also in 1802. These two sets of observations relate to the very early adoption of refineries and are hence extremely important.

Bonnard (1804-5, p. 266-267) states: *'Le procédé généralement employé aujourd'hui, consiste à faire subir à la fonte une seconde fusion dans des foyers nommés fineris, assez semblables à nos feux d'affinerie, mais plus grands, et qui sont alimentés avec du coaks. Pour cet effet, après avoir cassé les pig-iron en morceaux de 50-60 livres pesans, on place un ou plusieurs de ces morceaux sur le coaks dont le foyer est rempli, et au-dessus du vent des soufflets. La matière se fond, et en passant devant la tuyère tombe dans le creuset, où le vent qui plonge continuellement brûle la presque totalité du carbone qu'elle contient, et où les scories qui la couvrent l'empêchent d'être en contact avec le combustible qui pourrait lui en fournir de nouveau. On ajoute ainsi successivement de nouveaux Morceaux de pig-iron au-dessus des charbons, à mesure que les premiers se fondent, et le creuset se remplissant de métal, les crasses surnageantes sont chassées par le vent des tuyères et s'écoulent naturellement par-dessus les bords du foyer.'*

De deux en deux heures, ou mêmes plus souvent, on débouche un trou qui existe au bas de la plaque qui forme la paroi antérieure du foyer, et la fonte coule dans des rigoles qu'on a préparées dans le sable pour le recevoir, et où elle se moule en saumons plus considérable que ceux qu'on forme au sortir des hauts fourneaux. On en fait deux à chaque coulée. On nomme cette fonte fine metal. Les ouvriers qui savent qu'ils doivent obtenir une fonte blanche, ou souvent soin de donner aux saumons une forme large et peu épaisse, et de les arroser de beaucoup de l'eau, afin de rendre leur cassure aussi blanche que possible par un refroidissement plus subit.'

[The method generally used today, is to submit the cast iron to a second melting in a hearth named a finery, quite similar to our refinery fires, but larger, and fuelled with coke. For this purpose, after the pig iron has been broken in pieces of 50-60 pounds, one or more of these pieces is placed on the coke, with which the hearth is filled, above the bellows blast. The material melts, and falls into the crucible, passing the tuyère where the wind continually burns almost all the carbon that it contains and where the slag cover then prevents it from being in contact with the fuel that could provide it again. New pieces of pig-iron are successively added over the coals, as the first melt, the crucible fills with metal, the supernatant dross is driven by the blast of the tuyères and flows naturally over the edges of the hearth.

Every two hours or even more often, a hole that is at the bottom of the plate which forms the anterior wall of the furnace is opened, and the melt flows through channels that were prepared in the sand to receive it, and it moulds itself into pigs that are larger than those formed at the blast furnaces. They make two at each casting. This pig is called fine metal. Workers know they must make a white cast iron, by giving the pigs a broad and thin shape, and they sprinkle them with plenty of water to render their fracture as white as possible by sudden chilling.]

To this description O'Reilly (footnote p 149-150) added a gloss: *'Cette méthode est celle de Merthyrtydvil; en Staffordshire, le mouleur leur donne la forme d'une longue plaque de trois pieds de large sur une longueur égale à la quantité de fonte dans le coulée, et qu'il estime produire l'épaisseur de trois pouces environ; le fondeur jette de temps au temps après le coulée quelques seaux d'eau, afin de rendre la surface de cette plaque très-spongieuse; il estime avoir bien réussi, lorsque la fonte est blanche dans la cassure et aussi poreuse qu'il est possible.'*

[This is the method of Merthyr Tydvil; in Staffordshire, the founder gives them the form of a long plate three feet wide with a length equal to the amount of iron in the tap, and he tries to produce a thickness of around three inches; from time to time after the casting the founder throws a few buckets of water to make the surface of this plate very spongy; he considers himself successful when the cast iron has a white fracture and also is as porous as possible]

Bonnard provides the reason for the refinery as being that the iron is too carburised to refine in a single operation.

Hasenfratz (1812) provides a good account of early refineries, based largely on those by de Bonnard (1804-5) and O'Reilly (1805). Hasenfratz's description is reproduced in full here, because, although it is a derivative account, it summarises these two sets of observations relating closely to the period of foundation of Ynysfach ironworks: *'Les affineries dans lesquelles on fait la première opération diffèrent peu de celles dans lesquelles on traite la fonte au charbon de bois; seulement quelques-unes ont deux tuyères et deux porte-vents.'*

Après avoir cassé des saumons de fonte, en morceaux de 50 à 60 livres, ces fragments sont placés sur le charbon de houille, dont le fourneau d'affinerie est rempli. La chaleur, dégagée du combustible, mise en activité par les machines soufflantes, fond le métal qui tombe goutte à goutte, devant la tuyère, où le vent brûle une partie de son carbone; la fonte se réunit au fond du creuset, elle se couvre du peu de scories que les morceaux de saumon contenaient, auxquels se combine une partie de fer oxidulé qu'elles peuvent dissoudre.

La tuyère étant très-inclinée, produit deux effets: 1^o le métal se rougit, fond lentement, et s'oxidule par sa longue exposition à l'air; la partie supérieure du fourneau (celle où le fer est placé pour être fondu) est un peu échauffée; 2^o elle chasse, par-dessus les bords du foyer, les scories liquides qui recouvrent et oxidulent le métal, lorsqu'étant fondu, ce dernier est directement exposé au vent des machines soufflantes.

Dès que le creuset est suffisamment rempli de fonte fluide, on débouche le trou du chio, placé dans le fond du creuset pour faire couler le métal, et alors on continue de fondre des fragments de nouveau saumon.

Le fonte coule dans des moules creusés dans le sable: ce sont des creux ou des rigoles plus ou moins larges, et dont le fond est dressé et plane. Dans le Staffordshire, ils ont 3 pieds de long sur 3 de large, et 3 pouces de profondeur,

On jette sur cette fonte, immédiatement après la coulée, plusieurs seaux d'eau froide, pour rendre la surface spongieuse, la refroidir, la tremper, la rendre fragile, et lui donner une cassure blanche. Qui est un peu brillante, mais très-peu écaillée; ce qui prouve, d'après les observations de Réaumur, qu'elle contient encore beaucoup de charbon.

Il est bon d'observer ici que cette première opération, faite avec du charbon de houille, ne paraît pas donner de mauvaise qualité au fer, qui provient de la fonte traitée au haut fourneau; ce qui doit faire présumer qu'il serait possible d'obtenir de bon fer, en traitant, en affinant de bonnes fontes avec du charbon de houille, au lieu de charbon de bois.

Les plaques de fonte spongieuse qui proviennent de cette opération, porte le nom de fine métal. On consume environ une livre de charbon de houille pour obtenir une livre de plaque coulées; il se brûle beaucoup de fer dans cette fusion, car il faut, d'après les observations de l'ingénieur en chef de Bonnard, 110 à 112 parties de fonte, pour en obtenir 100 de plaques, et O'Reilly dit, que l'on emploie 115 parties de fonte à Cyfarthfa, et 120 à Bradley, pour produire 110 parties de fine métal: on passe environ 15 quintaux de fonte en six heures dans ces foyers; ce qui fait 6 milliers par vingt-quatre heures.'

[Refineries in which the first operation is made are little different from those in which charcoal iron is treated; only a few have two nozzles and two blast pipes.

After breaking the pig iron into 50 to 60 pound pieces, these fragments are placed on the coke with which the hearth of the refinery is filled. The heat, raised from the fuel by the activity of the blast, melts the metal which drips in front of the tuyère, where the blast burns part of its carbon; the melt accumulates at the bottom of the crucible, where it is covered by the small amount of slag from the pig iron which combines with and dissolves some of the oxidised iron.

The nozzle being very inclined has two effects: 1st the metal reddens, melts slowly, oxidises in its long exposure to the air; the upper part of the furnace (in which the iron is set to be molten) is only a little heated; 2nd it chases, to the edges

of the structure, the liquid slag covering and oxidising the metal, when, when melted is directly exposed to the blast.

Once the crucible is filled with enough fluid iron, the hole in the bottom of the crucible is opened for casting the metal, and then melting new fragments of pig continues.

The cast iron flows into moulds dug in the sand: they are hollow or channels more or less wide, of which the bottom is flat and smooth. In Staffordshire they are 3 feet long by 3 wide and 3 inches deep.

Immediately after the casting, several buckets of cold water are thrown onto the iron, to render the surface spongy, to cool it, to make it brittle and give it a white fracture, which is a bit bright, but not very scaly, which proves, according to the observations of Réaumur, that it still contains a lot of carbon.

It is good to note here, that this first operation, made with coke, does not appear to give poor quality iron from pig from the blast furnace; it must be assumed that it would be possible to get good iron by refining good cast iron with coke instead of charcoal.

The spongy iron plates that come from this operation are called fine metal. It consumes about a pound of coke per pound of plate castings; it burns a lot of iron in the reaction, agreeing with the observations of the Chief Engineer de Bonnard, that it requires 110 to 112 parts of pig iron to obtain 100 of plates, and O'Reilly said that at Cyfarthfa 115 parts of pig are used, and 120 at Bradley, to produce 110 parts of fine metal: they process about 15 quintals in six hours in these places, which makes 6 thousands per twenty-four hours.]

Rees (1811, 187-188) provided the earliest comprehensive English language account of a refinery; this bears marked differences to later descriptions, but many similarities with Bonnard's:

'the first step in the process of decarbonization, according to the more common mode of operating, is to expose the iron in a furnace, called by some a refinery, but by others, to distinguish it from one hereafter to be described, as a run-out furnace. It consists of a vessel open at the top, embedded in stone or brick work, about two foot three inches long, two feet wide, and ten inches deep. This is generally, in part, constructed of cast iron; and when so made, has an outer case about two or three inches distant from the inner one, which is constantly supplied with a stream of cold water to prevent the apparatus from melting. The iron to be decarbonized is placed in this receptacle, and kept in a continual state of fusion for three or four hours by the aid of a coke fire, which is heaped to a considerable height above the level of the vessel, and extended proportionally on the hearth that surrounds it. The size of the hearth is mostly about three yards in length, from two to three wide, but is completely covered by the funnel of the overhanging chimney. Bellows of considerable size are employed to carry on the process; and the current of air which issues from them is directed immediately on the surface of the iron by one or more tuyères. These tuyères are double, like the case, and continually cooled by the application of the same means. When the decarbonisation is completed, the metal is let out of an opening in the side, which has been kept close during the operation by a stopping of sand. It flows into a groove about 18 inches wide, and six or seven feet long, constructed of stone in the floor that surrounds the furnace.'

Dufrénot and Beaufort (1828, p. 467-468; based on a visit of 1823) described a single refinery with 2-3 water-cooled tuyères, and with a single brick wall on the side of the tuyères. They say the metal was run out into a trough, but give no details (although the end of a metal trough appears

to be illustrated in their figure, Plate XIV). The chimney was described as being supported on cast iron pillars. They illustrate the refinery well in Plate XIV. It has a large cast iron hearth only slightly offset towards the single row of three tuyères, it has hanging protective plates on the open sides. Thus, by 1823 many of the features characterising the later refineries are already present.

The Encyclopaedia Britannica supplement to the 4th, 5th, and 6th edition volume V (1824) describes refining rather fleetingly, but illustrates the refinery well in Plate LXXXIX, which shows a refinery (running out fire) with two tuyères on one side, iron columns supporting the chimney and the crucible of the hearth on one side of the overall hearth structure. The casting arrangements are not depicted.

Coste & Perdonnet (1830) produced an update to work of Dufrényot and Beaufort (1828). They note (p102-103) that fineries by then commonly had four or even six tuyères. They describe the trough as 2.74-3.05m long and 0.45m wide. They say that it was only closed with sand at the distal end to make raising the plate of finers metal easier. Their illustration of this type of refinery (Plate VI, Figures 1-3) is labelled '*finerie du Staffordshire*'.

Herbert (1836) illustrated a furnace that is identical to that figured by Rees (1811), but his account, reproduced here in full since it is of a period close to the construction of the Ynysfach enlarged refinery, contains much that is present in the later descriptions:

'The refining of pig-metal is a modern intermediate process of conversion, which the experience of our iron masters has led them to believe is the best economy in the preparation of the metal for subsequently rendering it malleable in the puddling furnace; although it is well understood not to be indispensable to the production of wrought iron. The furnaces employed for this purpose are small buildings, termed refineries; a vertical section of one of them is given in the cut on the next page, a is a thick cast-iron trough, having three of its sides made double, with a hollow space between, around which water is caused to flow from an external cistern b, the cooling effect of the fluid serving to prevent the fusion or other injury of the metal sides of the furnace by the intense heat; at c (in a line) are two pipes, through which air is forced from a blowing machine upon the materials in the trough; these pipes are kept cool by a constant stream of water always flowing over them, brought on by small pipes d, regulated by cocks. The bottom of the furnace is of brick, on which the fuel is laid, and over it the pigs to be refined. The building is surmounted by a wide chimney about 12 feet high, and the front, which is left open, has a projecting roof to cover the workmen who attend to it. In Wales it is usual to make these furnaces what is termed double; that is, the fire is somewhat larger though single, but the blast is double, there being usually three pipes and tuyeres on each of two. opposite sides of the furnace; each of the pipes are generally about an inch in diameter, and supplied with a blast equal to about 2 or 2 1/2 lbs. pressure upon the square inch.

The pigs are kept in a state of fusion for some time, exposed to an intense heat from the powerful blast just mentioned, which drives off a portion off the carbon united to the metal.

When the operation, which usually occupies two hours, is deemed to be complete, a hole in front of the hearth is tapped, through which the liquid metal flows into a very thick oblong flat mould of cast-iron, placed over a cistern of water; this causes the metal to be rapidly chilled, which is thus brought into a cake about 2 feet broad and 20 feet long. This plate of metal is extremely brittle, and presents on its fracture a silvery whiteness: it weighs about a ton. In some refineries the furnace is lined with firebricks or stones, without water running round it, and the refined metal is cast

upon sand in shallow moulds or depressions, and water is then thrown upon the metal to cool it quickly. As inattention or neglect on the part of the refiner would be productive of serious loss to the iron master, he is always paid according to the metal produced. Great experience and practical skill are requisite qualities in a refiner; his occupation is one of great personal exertion, and he is exposed to an intense fire, that no one unaccustomed to it could even approach.

He puts the charge of pigs upon the fire, attends to the progress of the melting, supplies the fire from time to time with coke, frequently stirring it up to equalize the heat; sees that the tuyeres are in good order, and that the water circulates uninterruptedly; runs out the metal when it is ready; he removes the plate from its mould when it has a little cooled, by means of a lever, on to a truck, and wheels it out of his shed; he then prepares his mould for the next plate, removes his cinders, and repeats the operation. The quantity of refined metal thus produced by a "double" furnace in Wales, is from 60 to 70 tons per week, of 6 days of 24 hours each, the men working in turns of 12 hours at a time, and 12 hours rest. The refiner selects his materials according to the quality of iron wanted. The best quality is from the dark grey pig, or No. 3, and the inferior sorts from bright, mottled, and white in their order. The very "worst" white iron cannot be used by itself in the refinery; being almost infusible from its deficiency of carbon, it is disposed to clog and settle on the hearth. To work up such iron in the refinery, it is mixed with pigs of a "better quality," or those containing more carbon, the union conferring fusibility.

When No. 3 pigs are used, it requires about 22 1/4 cwt. of them to produce one ton of refined metal; the "yield" however varies, from causes before adverted to, according to the degree of carbonation of the pig metal employed, the quality of the coke, the management of the blast, and various other circumstances. This reduction of weight is however not an entire loss, as a quantity of "cinder" is produced which floats on the top of the metal, and detaches itself as it cools; this cinder contains usually about 50 per cent, of its weight of iron, which is recoverable on the blast furnace.

Dufrényot *et al.* (1837) produced a third French report on the British industry. The section on refineries is largely as in the 1830 version, but they now describe the refinery trough as 4.57 to 6.10m long and 0.61m wide.

In the first three editions of his Dictionary, Ure (1839, 1840 and 1843) provided essentially identical descriptions of a refinery with two or three double tuyères on one side. He gives the chilling trough as 10 feet long, 3 feet broad and 2-2.5 inches deep. The illustration is of a slightly asymmetric hearth, with a slight ledge on side away from tuyères.

Overman (1851) described 4 tuyères as being normal (2 each side) or two double tuyères on one side. He gave the dimensions of the chilling trough as 10 feet in length, 30 inches in width and four inches in depth. A charge of 500-600 pounds of iron is quoted. He illustrates a brick built furnace with tuyères both sides. Overman may not have been describing current British practice, however. Overman disliked the refinery process and says (p. 256):

'The necessity of an intermediate process will readily be admitted: but a more awkward and unprofitable invention than that we are considering could not have originated from the most unskillful intellect. The apparatus is so worthless as scarcely to deserve notice. In fact, when we see the large amount of iron which is converted into slag; when we see the best charcoal iron wasted by the Western manufacturers, we are justified, we think, in wishing that this apparatus had never been invented. But the invention exists, and there is no immediate prospect of getting rid of it; therefore it is our duty to record its existence, and to exhibit its construction.'

Phillips (1854) described 6 tuyères (3 each side), with the cast plate formed in the chilling trough as 10 feet long, 2.5 feet broad and 2-2.5 inches deep, with 6 pigs (1 ton to 30 cwt) being the charge.

Truran (1855) describes the cistern as:

'At a sufficient distance below the inside floor of the refinery, and a few inches in advance of the dam plate, the casting bed or pig mould is constructed. A brick, or what is now preferable, and is now coming into general use, a cast iron cistern about 30 feet long, 4 feet wide and 2 feet deep forms the substructure. The casting bed is formed of thick cast iron blocks about 31/2 feet long, the same in width, and 6 to 9 inches thick, having side flanches to rest on the edge of the cistern underneath.'

The 5th and 6th editions of *Ure's Dictionary*, (Hunt 1861, 1867) were also updated to show three tuyères each side and to describe a charge of 2 tons. It shows a slightly asymmetric channel from hearth to trough (this is identical to the arrangement in Overman 1851).

Truran (1863) gave the dimensions of the chilling trough cistern as 30 feet long, four feet wide and 2 feet deep - and he describes an overflow notch to keep the water 1-2 inches below the base of the casting bed (which is 6-8 inches thick). He said there were 'single refineries' with 1 to 3 tuyères at the back and 'double refineries' with 2 or 3, rarely 4, tuyères on each side. His typical refinery consumed 2 tons of iron per heat. The drawings in this work and Percy's (see below) are of very similar structures. Truran also described something of the diversity of refineries - and the advantages of the 'running-in fire' developed at Dowlais to take molten iron direct from the blast furnace.

Percy (1864) provided a very comprehensive account of refinery operation, and amongst other useful details he stated:

'At the Cyfarthfa Iron-works of Messrs. Crawshay, in 1859, I observed refineries of two kinds: one with two twyers at the back and none at the sides, and the other with two twyers on each side and none at the back.'

Percy's main description of the refinery was of one (in Birmingham) with three tuyères on each side. The charge is given as 1 to 1.1 tons. Although Percy described the construction of the trough and cistern, he did not give measurements for its length.

These accounts allow something of the development of the refinery to be understood - notwithstanding the obvious regional and even inter-works variation. The early accounts (O'Reilly 1805, Rees 1811) all refer to casting wide pigs or plates onto sand or stone. The first indication of a metal trough is suggested by Dufrénot & Beaufort (1828, Plate XIV), which was derived from observations made in 1823.

Several descriptions of refineries give the length of the trough as 10 feet (Coste & Perdonnet 1830, Ure 1843, Overman 1851, Ure 1861). Phillips (1854) described the plate of finers metal as being 10 feet long, but does not indicate this as the length of the trough. Others suggest a longer trough was in use (15-20 feet, Dufrénoy *et al.* 1837; 20 feet Herbert 1836; 30 feet, Truran 1855, 1863).

These figures and dates suggest that cast iron troughs were probably introduced between 1811 and 1823. Truran still described cast iron troughs with cisterns as '*now coming into general use*' in 1855. The earliest reference to a long trough is in 1836. It seems likely that the preserved 21 feet long trough at Ynysfach is a design of the mid-1830s at the earliest, but probably rather later.

The implementation of refineries by the Crawshays may also be partially documented through their artistic

representation. Unfortunately none of the Turner sketches of 1798 show the refinery at Cyfarthfa clearly. The refinery building at Cyfarthfa was illustrated in c. 1797-1801 by Pamplin (the date of this is currently uncertain, pending on-going research: the illustration shows four blast furnaces in blast and this may have only been the case for a short period after construction of Furnace 4 in approximately 1797; visitors report only two in blast at Cyfarthfa in the period 1803-1805, by which date Pamplin had moved to London). The 1811 drawing for Wood's 'Rivers of Wales' was from the same perspective as one of the Turner sketches and again the refinery is difficult to identify, but possibly shows as a vertical gable wall. Penry Williams illustrated the Cyfarthfa site in c. 1817 and the Ynysfach site in c. 1819. A subsequent drawing of Merthyr Tydfil of 1847-1850 shows the northern section of the excavated Ynysfach refinery.

The Pamplin sketch of c. 1800 shows the refinery as a hipped-roof structure, with a colonnaded front and chimneys indicative of four refinery furnaces. The Wood drawing may suggest that the refinery had by then been reconstructed with a vertical gable wall and Rev. Sir Thomas Cullum who visited the works in 181 described 'six fineries blown by engines' (Birch 1967, p. 78). The Williams painting of c. 1817 was undertaken immediately after the great reconstruction of Cyfarthfa works (in the year that William Crawshay took full control of the works). This shows that the old refinery had certainly been replaced by this date; in its place was a typical Crawshay building - with three arches in the gable wall, three circular piercings above, and probably with arches in the front wall. The number of chimneys is obscured by the smoke, but appears probably to be five, to match the five blast furnaces. Williams' painting of Ynysfach works, of possibly slightly later date (usually dated to c. 1819) shows a small refinery building to the south of the two blast furnaces. This has an arched east wall and would appear likely to have housed two refineries (again matching the number of blast furnaces). The 1847-1850 drawing shows the Ynysfach refinery (the northern section of the excavated building), with a five-arched eastern wall and chimneys indicating two refineries.

Later evidence is provided cartographically. The 1851 Board of Health maps show the Cyfarthfa refinery as a 'Melting House', but does not illustrate its run-out troughs. By the time of the 1st Edition OS (mapped c.1870), the Cyfarthfa refinery has an expanded footprint with seven run-out troughs illustrated (suggesting the 1851 map showed a structure with only five refinery furnaces, presumably the structure illustrated 34 years earlier by Penry Williams). The run-out troughs are illustrated as extending 5.5m outside the building and as being 1.9m to 2.4m wide (perhaps suggesting that the map has included adjacent floor plates in that dimension).

At Ynysfach, the 'early' refinery building first appears in outline on John Wood's map of 1836. The refinery is labelled on the 1851 Board of Health map as 'refinery furnaces' and is in its enlarged state, with the six run out troughs all illustrated. The Ynysfach refinery building is essentially identical on the 1851 and 1870 maps except that the troughs are all shown as being the same length on the 1851 map, whereas they are illustrated as being different lengths on the 1st Edition OS. For the excavated trough, the length shown on the OS appears to include the area above the brick floor to the east of the trough (possibly the slag pit area), so the apparent lengths of troughs on the map may not convert to real lengths of the cast iron structure.

A tentative chronology of the Crawshay refineries in Merthyr Tydfil might be:

For Cyfarthfa

1. c. 1790 – certainly before 1817 and probably before 1811: hip-roofed building with four internal refineries, casting onto sand.
2. c. 1808 – c1851/70: gable-ended building with five refineries with metal troughs.
3. 1851/70 – 1879: gable-ended building extended to seven refineries with long metal troughs.

<i>Silice</i>	0,276
<i>Protoxide de fer</i>	0,612
<i>Alumine</i>	0,04
<i>Acide phosphorique</i>	0,072

1,000

On remarquera d'abord que ces scories ont beaucoup d'analogie par leur composition avec les scories de forges ordinaires; mais ce qu'elles presentent sur-tout de remarquable c'est l'existence de l'acide phosphorique en proportion considerable, circonstance qui avait été révoquée en doute par quelques personnes, et notamment par M. Jefstroem de Fahlun. Cette analyse fait voir combine est utile, sur tout pour le traitement des minerais phosphoreux, comme le sont généralement ceux des huillères, cette operation laquelle la fusion est complete."

For Ynysfach

1. c. 1805/19 – c. 1836: a small refinery to S of blast furnaces. Two refinery furnaces, probably casting to metal run-out troughs.
2. c. 1836 to c. 1850: refinery to E of old casting house. Two refinery furnaces with metal troughs.
3. c.1850-1879: enlarged refinery with six furnaces with long metal troughs.

[A slag coming from a refinery in the Dudley area has been analysed by M. Berthier, with the following result:

<i>Silica</i>	27.6%
<i>Protoxide of iron</i>	61.2%
<i>Alumina</i>	4%
<i>Phosphoric acid</i>	7.2%

100%

3.c. Contemporary understanding of the refinery

The new information about, and interpretation of, the refinery process is the central outcome from this project. Contemporary analysis of refinery materials is very limited. The earliest analytical study was that published by Dufrénoy and Élie de Beaumont (1828; see also above). They provided detailed descriptions of the refinery process and stated (when talking about problems with puddling):

'M. Cort parvint à éviter cette incertitude, en faisant precede le travail du fourneau à réverbère, qu'il appeal puddling, par une espèce de raffinage au coke. Le but de cette operation était de décarburer la fonte et de la preparer à devenir malleable. Le étal prit alors le nom de finer metal, metal plus fin, que l'on appelle pur abrèger FINE-METAL.'

[*Mr. Cort managed to avoid this uncertainty, by preceding the work of the reverberatory furnace, which he called puddling, by a kind of coke fining. The purpose of this operation was decarburize the cast iron and to prepare it to become malleable. The metal then took the name of finer metal, called for short fine metal.*]

In pages 496-497 they provide a detailed description of the use of the refinery (which is very similar to other contemporary accounts, but also provide a commentary on the nature of the slag:

'Les scories sont noires, un peu métalloïdes, souvent fibreuses et cristallines, beaucoup moins cependant que celles qui proviennent des opérations postérieures. Ces scories sont produites seulement par celles que contenait la fonte qu'on soumise a cette operation, et par la scorification des terres qui entrent dans la composition de la houille. Quelquefois, quand la fonte est de mauvaise qualité, on fait une légère addition de calcaire.'

[*The slags are black, a bit metallic, often fibrous and crystalline, but much less so than those from the previous operations. These slags are produced only by those that are contained within the iron subjected to this operation, and the slagging of those earths which are components of coal. Sometimes, when the pig iron is of poor quality, there is a slight addition of limestone*]

They also sent samples of slag to Berthier for analysis (Pierre Berthier was Professor of Assaying and the chief of the laboratory at the École des Mines in Paris). Their commentary upon his analysis was far in advance of similar commentaries by the British authors of the period:

"Une scorie provenant d'une finerie des environs de Dudley, analyse par M. Berthier, a donné pour résultat:

It will be observed that the slag is very analogous in composition with slag ordinary forges, but that they have most remarkably is the existence of phosphoric acid in considerable proportion, a property which had been doubted by some people, including Mr. Jefstroem of Fahlun. This analysis see how useful, especially for the treatment of phosphatic ore, as are generally those of the coalfields, is this operation which completes the smelting."

In contrast, the early British accounts of the refinery make little or no reference to phosphorus at all.

Rees (1811, p. 188) in common with many others appears to have though decarburisation the main purpose:

'The total quantity of carbon which the iron contains is not estimated at more than 1/25th; and yet the approach of it to the pure state, or, in technical language, to the state of bar or wrought-iron, after this operation, is very inconsiderable.'

He also optimistically stated on the following page (p.189): *'The art is still in its infancy; and the light of chemical science, by being brought to focus here, cannot fail to disclose may improvements in the present modes of procedure, which will greatly abridge the expence now incident to this valuable branch of national industry. That the mere abstraction of about 4 per cent. of carbon should require a sacrifice of 40 per cent. of iron, appears monstrous beyond example: and as those who are connected with the art become more scientific in their views, we shall unquestionably find that it will become more economically accomplished.'*

However, Phillips (1854) still described refining as causing the metal to *'lose a considerable portion of its carbon, and nearly the whole of its silicium'*.

Truran (1855, p. 128) provided a rather similar view: *'hence, in refining, the object in view is not so much to deprive the iron of the cinder alloy, except in cases where this is of a prejudicial quality, as to decarbonate the iron. If depriving it of the alloy was the object of refining, as is commonly supposed, the grey varieties having the least amount would be refined with facility instead of difficulty',* but he also noted:

'It is generally known that the lean carbonates abounding largely in silica produce finished iron of a cold-short

character. The addition of lime in moderate quantities appears to neutralize this tendency, and the resulting iron is comparatively free from the opposite extreme- red short.'

The analyses of irons before and after refining given by Truran show the following:

	Crude Iron	Refined plate metal
Iron	95.26	98.33
Carbon	2.63	0.87
Silicium	2.38	0.53
Aluminium	0.73	0.26
Phosphorus	Trace	Trace
Sulphur	Trace	Trace

Rogers (1858) discussed the chemistry of refining at some length (Chapter XVIII) and was aware of the role of the refinery in removing 'metalloids' from the pig iron. He states (p. 213):

'This fusion of the pig oxidates a large portion of the alloying bodies and the, forming a black scoria or cinder, in which the oxide of iron greatly predominates; this cinder then reacts upon the melted metal under operation, and separates more of the alloys in question'

and (p. 216):

'the metal from the good pigs has now parted with the greater portion of its carbon and silicium, probably not retaining so much carbon as steel of the lowest gradation, i.e. 1-200th part (which steel will possess nearly all the properties of the best wrought-iron, with the addition of great elasticity also), and yet this refined metal will be brittle, hard and non-weldible; and manifestly for the principal reason, the whole of it is still an alloy of silicium, carbon, and iron, although these alloying bodies will certainly be in less proportions than in the pig'

Here is an increasingly recognisable chemical approach to trying to understand the processes, but it is constrained by a lack of understanding of the composition of, particularly, white cast iron.

Percy (1864) described reduction in the concentrations of both silicon and sulphur in the refinery, but clearly believed decarburisation was the main purpose and expressed surprise at the unexpectedly high carbon content of the finers metal whose analysis he presented (p. 626).

Truran took great care over the discussion of problems with the mass balance of the refining process, but as far as the chemical process is concerned he referred mainly to reductions in silicon, quoting (p. 204; some *'analyses of French iron by a Continental chemist'*) a reduction of silicon from 4.5% to 0.5%, of carbon from 3.0 to 1.7% and phosphorus from 0.2% to undetectable.

Bell (1884) provided the first 'modern' chemical description of refining when he stated:

"Mr Edward Williams informs me that the use of the "sand bottom" had been generally abandoned before he was old enough to remember much of its peculiarities. His impression is that it did its work badly; because it was necessary to avoid the accumulation of fluid cinder, rich in the oxide of iron, which in puddling, as in refining, is the agent which effects the removal of phosphorus, could not fail to damage the quality of the product. To some extent I apprehend this evil would be counteracted by previously passing the pig iron through the refinery, and by the time required in puddling "a heat" which occupied three hours."

3.d. Iron smelting at Ynysfach

The blast furnace slags analysed for this project are rather more difficult to assign with any certainty to a particular phase of activity.

Iron sample YSF18 and slag YSF17 both come from a single 'end-of-tap' runner. Because of this, their compositions need to be considered as possibly atypical of the bulk materials. None the less, their composition is remarkably different from the other blast furnace materials (both slag and pig iron) considered here. The iron and slag are both phosphoric and display evidence for a low-magnesium flux (and a corresponding pseudowollastonite- rather than melilite- dominated mineralogy). These materials are much close to published analyses of blast furnace slag from Dowlais in the 1850s (Percy 1864). They are interpreted as residues produced at an earlier period than those described in the following paragraphs – and are therefore likely to be materials from Ynysfach.

The main group of analysed slags are a coherent suite of materials characterised by a high Mg:Ca ratio and a compositional trend precisely focused on the point of maximum fluidity and sulphur-trapping potential in the MgO-CaO-SiO₂ system. This composition is quite different from contemporary accounts of blast furnace slag composition in the Merthyr Tydfil ironworks of the 1850s.

Of these, samples YSF21 and YSF24 have low to moderate levels of phosphorus. YSF24 is also associated with an inclusion of grey cast iron with a high phosphorus content – which is therefore not from a process to produce Bessemer pig. It would seem likely that these slags pre-date the steelworks phase, and therefore that they possibly be from Ynysfach itself. They provide interesting evidence for a change in fluxing material prior to the steelworks period.

Samples YSF19, YSF20, YSF22 and YSF23 all have extremely low phosphorus and there must have been smelted with low-phosphorus iron ores. These may possibly therefore, but not necessarily, belong to the steelworks phase of the Cyfarthfa site. Such a composition might, however, have been produced at a slightly earlier date as the works became increasingly reliant on imported haematite ore in the third quarter of the 19th century.

3.e. The Cyfarthfa Steelworks

The materials definitely associated with the steelworks phase of the Cyfarthfa complex include pig iron of the composition produced as feed for the acid Bessemer process (YSF15, YSF16), examples of tuyères for Bessemer converters and slag from the acid Bessemer process (YSF6, YSF7). As stated above, the blast furnace slags YSF19, YSF20, YSF22 and YSF23 may be from the steelworks phase or slightly earlier.

It is assumed that these residues derive from Cyfarthfa, rather than Dowlais, the other steelworks of Merthyr Tydfil, because of the close association of Ynysfach with Cyfarthfa, even after Ynysfach ceased operating, with the railway south from Cyfarthfa to the Ynysfach Cinder Tips near Rhyd-y-car, and to Rhyd-y-car junction, passing through the derelict Ynysfach works. The Cyfarthfa steelworks was sold to guest Keen and Nettlefolds Ltd (owners of the Dowlais works) in 1902, and operated by them until closure in 1910 (with a subsequent short reopening in 1915-1919). There is therefore a slight possibility that some dumping of waste from Dowlais might have occurred at this late period, but this seems geographically unlikely.

Conclusion

The analysis of the refinery residues is the first modern work on these materials. They have an unusual mineralogy dominated by metastable phosphoran olivine. There are several other phosphorus-bearing phases, demonstrating the role of refining in partially dephosphorising the pig iron.

Modelling of the mass balance for the reaction is not possible because of the many unknowns. It is clear that range of reducible elements has been at partially removed from the pig by the refinery. The most important elements in this group are silicon, manganese and phosphorus, but the mineralogy of the slag is also influenced by lesser amounts of vanadium and chromium.

Inspection of the accounts of the trials of Cort's process in the 1780s lead to a strong suspicion that elevated phosphorus may have been to blame for some of the poor results. Thus, although desiliconisation has been suggested to be the main role of the refinery in the past, dephosphorisation is suggest to be equally important, if not more so, by the present data.

The project has also demonstrated the significance of the microresidues associated with refining. The dominant form are slag spheroids that are distinguishable from other forms of previously described spheroidal archaeometallurgical microresidue and share a common composition with the macroresidues. A small class of spheroid, formed almost entirely of iron or iron oxide has also been identified for the first time. These two classes of material vividly illustrate the nature of the working environment of a refinery. They may also potentially illuminate the problems of trying to generate as mass balance for the reaction.

Investigation of the written sources for the nature of the refinery process has shown a rich suite of descriptions by French visitors, which represents a poorly used resource for English-speaking researchers of the period. The research demonstrates that the type of refinery excavated at Ynysfach is unlikely to be typical of a period before the late 1830s, which is in agreement with the evidence for the construction of the 'early' refinery in the late 1830s and of its extension in c.1850.

Although the focus of the project was on the refinery process, some analytical work was undertaken on blast furnace residues and these were suggest of an unexpected composition approaching the ideal for the system. A combination of the properties of the slag and properties of the associated iron suggests that these slags date to late in the life of Ynysfach Ironworks, probably from the 1860s or 1870s, but that most of the examined blast furnace slags pre-dated the steelworks phase of the Cyfarthfa complex.

The steelworks phase was represented surprisingly strongly in the residue assemblage, possibly including some blast furnace slags, but more certainly including examples of Bessemer pig, of Bessemer converter tuyères and of slags from the acid Bessemer process.

The project thus illuminates two periods of the development of iron making in Merthyr Tydfil when the presence of phosphorus in the ores created technological challenges. In the late 18th century the high levels of phosphorus may have been one of the reasons for the initial problems of Cort's puddling process which were rectified by the introduction of the refinery. In the 1860s to 1880s, the challenge to Merthyr was to adapt to the advent of bulk steelmaking, particularly after bulk steel eliminated the market for wrought iron rails in the early 1880s. Once again phosphorus in the ore prevented the adoption of the new Bessemer process (in its original acid Bessemer variant). Dowlais ironworks, a would-be early adopter of the Bessemer process bore much of the

brunt of the technological problems. By the time Cyfarthfa finally converted to steelmaking, it was clear that its implementation of the acid Bessemer process needed to be totally reliant on imported low-phosphorus ores.

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Figure Captions

Figure 1: Samples of blast furnace slags from Ynysfach: rare earth element profiles, normalised to Upper Crust (normalisation factors after Taylor & McLennan 1980).

Figure 2: Samples of blast furnace slags from Ynysfach: back-scattered electron photomicrographs of representative examples.

- YSF17 SOI1. Scalebar 200 μm .
- YSF17 SOI9. Scalebar 60 μm .
- YSF19 SOI6. Scalebar 600 μm .
- YSF19 SOI5. Scalebar 100 μm .
- YSF21 SOI1. Scalebar 200 μm .
- YSF21 SOI5. Scalebar 100 μm .
- YS22 SOI4. Scalebar 600 μm .
- YSF22 SOI8. Scalebar 100 μm .

Figure 3: Samples of blast furnace slags from Ynysfach: major element analyses by XRF plotted on $\text{SiO}_2\text{-CaO-MgO}$ diagram for $\text{Al}_2\text{O}_3 = 15\%$ (fields after Muan & Osborn 1963). Pale green tone indicates compositions fully liquid at 1500C. Green lines indicate liquidus isotherms. PWOLL = pseudowollastonite
MER = merwinite

Figure 4: Samples of cast iron from Ynysfach: back-scattered electron photomicrographs of representative examples.

- YSF13 SOI6. Scalebar 1mm.
- YSF13 SOI7. Scalebar 100 μm .
- YSF14 SOI2. Scalebar 600 μm .
- YSF14 SOI1. Scalebar 40 μm .
- YSF15 SOI6. Scalebar 700 μm .
- YSF16 SOI3. Scalebar 2mm.
- YSF24 SOI7. Scalebar 1mm.
- YSF24 SOI8. Scalebar 600 μm .

Figure 5: Samples of refinery slags from Ynysfach: photographs of macroscopic slags.

- YSF32, broken weathered face
- YSF32, cut face
- YSF5, cut face

Figure 6: Variation in EDS microanalyses of phosphoran olivine from refinery slags from Ynysfach. Graph of atoms per formula unit phosphorus against atoms per formula unit silicon.

Figure 7: Variation in EDS microanalyses of spinels from refinery slags from Ynysfach. Each graph shows the variation of titanium, vanadium, iron(II), iron(III), and chromium with aluminium (all displayed in atoms per formula unit with 4 oxygens in the modelled spinel composition). The upper diagram shows analyses from samples of 'normal' refinery slags; the lower shows analyses from the heavily-hydrothermally altered areas of samples YSF8 and YSF27.

Figure 8: Variation in EDS microanalyses of phosphoran iscorite from refinery slags from Ynysfach. Graph of atoms per formula unit phosphorus against atoms per formula unit silicon.

Figure 9: Samples of refinery slags from Ynysfach: rare earth element profiles, normalised to Upper Crust

(normalisation factors after Taylor & McLennan 1980). The upper diagram shows the profiles for 10 samples with variable enrichment of the middle REE with a tendency for the profile to flatten with increasing REE abundance; the lower diagram shows four samples with a flatter profile and an abundance at the upper levels seen in the group.

Figure 10: Samples of refinery slags from Ynysfach: back-scattered electron photomicrographs of representative examples (1).

- YSF2. SOI2. Scalebar 1mm.
- YSF2. SOI6. Scalebar 200 μm .
- YSF2. SOI8. Scalebar 40 μm .
- YSF2. SOI3. Calcium. Scalebar 40 μm .
- YSF2. SOI4. Iron. Scalebar 40 μm .
- YSF2. SOI5. Potassium. Scalebar 40 μm .
- YSF2. SOI6. Phosphorus. Scalebar 40 μm .
- YSF2. SOI8. Sulphur. Scalebar 40 μm .

Figure 11: Samples of refinery slags from Ynysfach: back-scattered electron photomicrographs of representative examples (2).

- YSF3. SOI9. Scalebar 100 μm .
- YSF3. SOI11. Scalebar 70 μm .
- YSF4. SOI2. Scalebar 600 μm .
- YSF4. SOI4. Scalebar 60 μm .
- YSF4. SOI7. Scalebar 80 μm .
- YSF4. SOI7. Aluminium. Scalebar 80 μm .
- YSF4. SOI7. Titanium. Scalebar 80 μm .
- YSF4. SOI7. Vanadium. Scalebar 80 μm .

Figure 12: Samples of refinery slags from Ynysfach: back-scattered electron photomicrographs of representative examples (3).

- YSF9. SOI3. Scalebar 600 μm .
- YSF25. SOI4. Scalebar 100 μm .
- YSF27. SOI7. Scalebar 600 μm .
- YSF27. SOI9. Scalebar 600 μm .
- YSF27. SOI10. Scalebar 100 μm .
- YSF29. SOI7. Scalebar 600 μm .
- YSF29. SOI8. Scalebar 600 μm .
- YSF29. SOI10. Scalebar 70 μm .

Figure 13: Samples of refinery slags from Ynysfach: back-scattered electron photomicrographs of representative examples (4).

- YSF27. SOI1. Scalebar 600 μm .
- YSF27. SOI15. Scalebar 200 μm .
- YSF27. SOI12. Scalebar 300 μm .
- YSF27. SOI13. Scalebar 70 μm .
- YSF27. SOI14. Scalebar 40 μm .
- YSF8. SOI7. Scalebar 800 μm .
- YSF8. SOI6. Scalebar 600 μm .
- YSF8. SOI8. Scalebar 60 μm .

Figure 14: Samples of refinery microresidues from Ynysfach: rare earth element profiles, normalised to Upper Crust (normalisation factors after Taylor & McLennan 1980). The grey tone shows the field occupied by the profiles of samples of macroscopic refinery slags (see Figure 9).

Figure 15: Bivariate graphs of EDS microanalyses from representative areas within particles of refinery microresidues from Ynysfach, plotted for comparison with similar analyses of samples of macroscopic refinery slags and possible puddling slags from Ynysfach.

Figure 16: Photograph of bulk sample of refinery microresidues (sample YSF11) from Ynysfach.

Figure 17: Samples of refinery microresidues from Ynysfach: back-scattered electron photomicrographs of representative examples. (1)

- a) YSF11a. SOI1. Scalebar 60µm.
- b) YSF11a. SOI8. Scalebar 60µm.
- c) YSF12. SOI9. Scalebar 400µm.
- d) YSF12. SOI10. Scalebar 100µm.
- e) YSF11. SOI31. Scalebar 600µm.
- f) YSF11. SOI32. Scalebar 60µm.
- g) YSF11. SOI28. Scalebar 2mm.
- h) YSF11. SOI27. Scalebar 100µm.

Figure 18: Samples of refinery microresidues from Ynysfach: back-scattered electron photomicrographs of representative examples. (2)

- a) YSF11. SOI43. Scalebar 1mm.
- b) YSF11. SOI44. Scalebar 100µm.
- c) YSF11. SOI41. Scalebar 1mm.
- d) YSF11. SOI42. Scalebar 100µm.
- e) YSF12. SOI28. Scalebar 30µm.
- f) YSF12. SOI28. Iron. Scalebar 30µm.
- g) YSF12. SOI28. Phosphorus. Scalebar 30µm.
- h) YSF12. SOI28. Silicon. Scalebar 30µm.

Figure 19: Samples of possible puddling slag from Ynysfach: rare earth element profiles, normalised to Upper Crust (normalisation factors after Taylor & McLennan 1980).

Figure 20: Samples of possible puddling slag from Ynysfach: back-scattered electron photomicrographs of representative examples.

- a) YSF30. SOI12. Scalebar 1mm.
- b) YSF30. SOI8. Scalebar 200µm.
- c) YSF30. SOI1. Scalebar 600µm.
- d) YSF30. SOI2. Scalebar 60µm.
- e) YSF30. SOI14. Scalebar 100µm.
- f) YSF31. SOI1. Scalebar 2mm.
- g) YSF31. SOI7. Scalebar 1mm.
- h) YSF31. SOI8. Scalebar 100µm.

Figure 21: Photograph of example of a tuyère from a Bessemer converter from Ynysfach. The tuyère fragment is from context 194

Figure 22: Samples of acid Bessemer slags from Ynysfach: rare earth element profiles, normalised to Upper Crust (normalisation factors after Taylor & McLennan 1980).

Figure 23: Samples of acid Bessemer slag from Ynysfach: back-scattered electron photomicrographs of representative examples.

- a) YSF6. SOI1. Scalebar 1mm.
- b) YSF6. SOI3. Scalebar 200µm.
- c) YSF6. SOI7. Scalebar 100µm.
- d) YSF6. SOI6. Scalebar 40µm.
- e) YSF6. SOI9. Scalebar 50µm.
- f) YSF7. SOI1. Scalebar 50µm.
- g) YSF7. SOI2. Scalebar 600µm.
- h) YSF7. SOI3. Scalebar 1mm.

Figure 24: Bivariate plots of EDS micronalyses of sillimanite in glass, in sample of clinker YSF1, from Ynysfach.

Figure 25: Sample of clinker from Ynysfach: rare earth element profile, normalised to Upper Crust (normalisation factors after Taylor & McLennan 1980).

Figure 26: Sample of clinker from Ynysfach: back-scattered electron photomicrographs of representative examples.

- a) YSF1 SOI1. Scalebar 600µm.
- b) YSF1 SOI2. Scalebar 60µm.
- c) YSF1 SOI12. Scalebar 40µm.
- d) YSF1 SOI10. Scalebar 100µm.
- e) YSF1 SOI5. Scalebar 60µm.
- f) YSF1 SOI6. Scalebar 600µm.

Tables

Table 1: Details of samples selected for further analysis.

Table 2: Major element analyses of samples by XRF, expressed in oxide wt%. LOI = loss on ignition. Iron expressed alternatively as Fe₂O₃ or FeO

Table 3a: Trace elements analysed by ICP-MS, expressed in ppm.

Table 3b: Trace elements analysed by ICP-MS, expressed in ppm. (contd.)

Table 4: EDS Micro-analyses of the constituent minerals of blast furnace slags.

Table 5: Major element chemical composition of BF slags

Table 6: Major element chemical composition of cast irons (normalised to 100% excluding carbon)

Table 7: Typical compositions of pig iron, in wt%, after Forsythe (1909, p. 287)

Table 8: Major element chemical composition of refining slags

Table 9: EDS Micro-analyses of the constituent minerals of refining slags (1): phosphoran fayalite.

Table 10: EDS Micro-analyses of the constituent minerals of refining slags (2): alkali-bearing phosphate.

Table 11: EDS Micro-analyses of the constituent minerals of refining slags (3): iron-calcium-manganese phosphates.

Table 12: EDS Micro-analyses of the constituent minerals of refining slags (4): phosphoran iscorite.

Table 13: Major element chemical composition of refining microresidues (sample YSF11)

Table 14: Major element chemical composition of refining microresidues (sample YSF11a)

Table 15: Major element chemical composition of refining microresidues (sample YSF12)

Table 15: Major element chemical composition of possible puddling slags.

Table 17: EDS Micro-analyses of the constituent minerals of possible puddling slags (1): phosphoran fayalite.

Table 18: EDS Micro-analyses of the constituent minerals of possible puddling slags (2): alkali-bearing phosphate.

Table 19: EDS Micro-analyses of the constituent minerals of possible puddling slags (3): iron-calcium-manganese phosphates.

Table 20: EDS Micro-analyses of the constituent minerals of possible puddling slags (4): phosphoran iscorite.

Table 21: Major element chemical composition of acid Bessemer converter slags

Table 22: EDS Micro-analyses of the constituent minerals of acid Bessemer converter slags

Table 23: Major element chemical composition of clinker

Archive Tables

Table A1: Major element analyses of samples by XRF, expressed in oxide wt%. LOI = loss on ignition. Iron expressed alternatively as Fe₂O₃ or FeO

Table A2: Trace element analyses of samples by XRF, expressed in oxide wt%.

Table A3a: Trace elements analysed by ICP-MS, expressed in ppm.

Table A3b: Trace elements analysed by ICP-MS, expressed in ppm. (contd.)

Table A4: Major element analyses of samples by ICP-MS, expressed in oxide wt%.

Table B1: EDS microanalyses expressed in elemental wt%. b.d. = element sought, but below detection limit

Glossary

- Acid Bessemer process:** the initial variant of the **Bessemer process** with a siliceous (acid) lining to the **Bessemer converter** vessel. This could only be used with iron with a very low phosphorus content.
- Air furnace:** largely synonymous with **reverberatory furnace**, although some early forms shared more with crucible furnaces.
- Åkermanite:** the calcium magnesium silicate end-member of the **melilite** group, $\text{Ca}_2[\text{MgSi}_2\text{O}_7]$.
- Anhedral:** a crystalline material which does not exhibit the development of any crystal faces, particularly when the crystal grows to fill void space left between pre-existing phases.
- Augite:** a **pyroxene** (clinopyroxene) mineral with a generalised formula of: $(\text{Ca,Na})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6$
- Austenite:** a high-temperature form of iron, known as γ -iron, which is first-formed phase during the crystallisation of a **cast iron**.
- Bar iron:** the principle form of iron produced by **conversion** forges during the early industrial period, initially produced by hammering, later by rolling.
- Bessemer converter:** a large tilting, rounded vessel for containing the reaction of the **Bessemer process**. Blown through numerous narrow-bore **tuyères** installed in its base (less commonly through lateral **tuyères**).
- Bessemer process:** a process for the bulk production of **steel**, by blasting air through molten iron in order to oxidise its impurities. Originally patented in 1856, it took another decade to overcome various problems and to be implemented on a large scale.
- Bessemer pig:** raw **pig iron** of a suitable grade for conversion to steel in the **Bessemer process**. In Britain this usually had an elevated silicon content, since the exothermic oxidation of silicon supplied much heat to the process.
- Blast furnace:** a large shaft furnace for the reduction of metal ores, employing a forced draught near the base.
- Bleb:** a small rounded particle or textural component, often a droplet or prill.
- BSEM:** backscattered electron microscopy; the backscattered electrons are formed into an image, with the amount of backscatter indicating the electron density of the target, hence imparting a compositionally-controlled greyscale to the image.
- Cast iron:** an alloy of iron with carbon with the carbon content being between 2.1% and 4% by weight.
- Cementite:** iron carbide, Fe_3C .
- Chafery:** an open, bellows-blown reheating hearth used for the working of the 'bloom' to produce bar iron. Usually the second stage in a charcoal-fuelled Walloon finery **conversion** forge, but also used of the hearth employed to **forge bar iron** in the final stage of the **potting and stamping** process.
- Chromite:** a chromium-bearing **spinel** group mineral; $\text{Fe}^{2+}\text{Cr}_2\text{O}_4$.
- Conversion:** a name for the process of transformation of **cast iron** into **wrought iron**.
- Cotectic:** crystallisation of a liquid to produce two phases at the same time.
- Coulsonite:** a vanadium-bearing **spinel** group mineral; $\text{Fe}^{2+}\text{V}_2\text{O}_4$.
- Cristobalite:** a high temperature silica (SiO_2) polymorph.
- Dendrite:** a branched crystal form, often associated with rapid growth.
- Dolomite:** a calcium magnesium carbonate mineral, $\text{CaMg}(\text{CO}_3)_2$, or more loosely a carbonate rock (limestone) rich in dolomite.
- Dry puddling:** **puddling** on a bed of sand; the original technique of Cort's patent of 1784.
- EDS:** Energy-dispersive spectrometry; an analytical technique to identify elements by their characteristic X-Ray emissions when subject to an incident electron beam, typically for microanalysis inside an **SEM**.
- End-member:** The limits of solid solution in a mineral system. Used in cases where all the possible sites which a particular element can occupy in a crystal are occupied by atoms of the element. An example would be **fayalite**, Fe_2SiO_4 being the iron end-member of the **olivine** group, whereas **forsterite**, Mg_2SiO_4 is the magnesium end-member.
- Enstatite:** a magnesian **pyroxene** (orthopyroxene), MgSiO_3 .
- Euhedral:** a crystal shape in which the crystal has developed its faces, indicating its growth was unobstructed by previously formed phases.
- Fassaite:** a variety of the **pyroxene augite**, with a low iron content; $\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$.
- Fayalite:** the iron-rich end member of the **olivine** group, Fe_2SiO_4 .
- Ferrite:** low temperature form of iron, α -iron.
- Fettle:** in foundry work, to finish a crude casting by removing excess metal. More general, to finish. In **wet puddling** the 'finishing' of the furnace was achieved by lining its base with materials such as hammerscale, roasted slag and iron ore, both to promote a protective slag and more importantly to supply oxygen for decarburisation.
- Finers metal:** **white cast iron** produced from a **refinery**. Usually cast into thin slabs.

- Finery**: most commonly used for the first hearth in a Walloon charcoal **conversion** forge, in which pig iron is decarburised by melting in a strong air blast. Also used for a building containing a finery hearth. Also used more generally for a variety of hearths/processes for decarburising iron in a hearth.
- Flourishing furnace**: an **air furnace** employed in **potting and stamping** for heating clay pots packed with iron and flux, so the iron can be decarburised without contact with the coal/coke fuel.
- Flux**: a material used to lower the melting point of another material. In early industrial iron making specifically used of the limestone or lime added to the charge of the **blast furnace**.
- Forsterite**: the magnesium-rich end member of the **olivine** group, Mg_2SiO_4 .
- Gehlenite**: the calcium aluminium silicate end-member of the **melilite** group, $Ca_2[Al_2SiO_7]$.
- Graftonite**: an iron, manganese and calcium phosphate: $(Fe^{2+}, Mn, Ca)_3(PO_4)_2$
- Grey cast iron**: a **cast iron** in which much of the carbon is present as graphite (as opposed to **white cast iron**).
- Hercynite**: an iron-aluminium member of the **spinel** group of minerals: $FeAl_2O_4$
- ICP-MS**: Inductively coupled plasma mass spectrometry: an analytical technique which ionizes the sample with inductively coupled plasma and then draws the ions into a mass spectrometer.
- Interstitial space** or **interstice**: the space between the main generation of crystals in a material. On cooling the main phase of crystals will solidify whilst the interstitial spaces are still occupied by molten material, which will solidify at a lower temperature.
- Iscorite**: the informal name for a phase (artificial mineral) to date only observed in metallurgical slags. The chemical composition is $Fe^{2+}_5Fe^{3+}_2SiO_{10}$. The mineral is typically encountered in contexts where **wustite** is oxidised in the presence of **fayalite**.
- Magnetite**: an iron oxide member of the **spinel** group, Fe_3O_4 .
- Melilite**: a mineral of the melilite group, whose end-members include **gehlenite** and **åkermanite**. The generalised formula for melilite is $(Ca, Na)_2(Al, Mg, Fe^{2+})(Al, Si)SiO_7$
- Metastability**: a state where a material may persist in a form which is not the thermodynamically most stable.
- Mullite**: an aluminium silicate, $Al_6Si_2O_{13}$.
- Oldhamite**: calcium sulphide, Ca_2S .
- Olivine**: a group of silicate minerals of the form $(M^{2+})_2SiO_4$ where M can commonly be iron, magnesium, calcium (up to half the M^{2+} ions) or manganese. Includes the end-members **fayalite** (Fe_2SiO_4), **forsterite** (Mg_2SiO_4), tephroite (Mn_2SiO_4), kirschsteinite ($CaFeSiO_4$) and monticellite ($CaMgSiO_4$). The complex substitutions are described in this report by using the convention of describing the Fe-Mg as the fayalite-forsterite proportion (for instance Fa95Fo5, where Mg is 5% of the total of Mg+Fe) and then describing the Ca and Mn concentrations as percentage substitutions of the forsterite-fayalite.
- Paragenesis**: a mineral assemblage. The paragenetic sequence is the succession of phases formed during crystallisation.
- Pearlite**: a structure of intergrown **ferrite** (88%) and **cementite** (12%) formed by cooling **austenite** in a eutectoid reaction.
- Phosphoran iscorite**: this name is proposed here for **iscorite** containing more than 0.03 atoms per formula unit (10 oxygens); definition created by analogy with that for **phosphoran olivine**.
- Phosphoran olivine**: **olivine** containing phosphorus substituting for silicon to more than 0.03 atoms per formula unit (4 oxygens) (Boesenbery & Hewins 2010)
- Pig**: an ingot of **cast iron**, usually used when cast direct from the **blast furnace**. Named for the supposed resemblance of the feeder and ingots to a sow and piglets.
- Pig boiling**: A late version of **puddling**, in which sufficient oxygen is included within the charge (in roasted slag, hammerscale, iron ore and scrap metal) that the melt appears to boil as gas is evolved during decarburisation.
- Pig iron**: a name given to raw **cast iron** produced from the blast furnace and usually cast into **pigs**.
- Potting and Stamping**: an 18th century **conversion** process, involving melting **pig iron** in an oxidising environment, **stamping** the resultant **cast iron** into small fragments which were packed into clay pots with **flux** for decarburising in a **flourishing furnace**. When the pots broke, the iron could be worked in a **chafery**.
- Prill**: a small aggregate of a material, either a spheroidal droplet or a runnel, formed from a melted liquid and either occurring as a discrete particle or as an inclusion within another material.
- Pseudoternary diagram**: a ternary diagram where the displaying part of a system of more than three components
- Pseudowollastonite**: a high temperature polymorph of the calcium silicate $CaSiO_3$.
- Puddling**: a process for **conversion** of cast iron to wrought iron by decarburising in a **reverberatory furnace** (puddling furnace). The original process patented by Henry Cort in 1784, was later known as **dry puddling** and used a sand bed; later **wet puddling** used an iron oxide rich fettling on an iron base to allow a slag to be held in the furnace. Wet puddling subsequently evolved into **pig-boiling** in which sufficient oxidising sources were present to produce a very vigorous reaction.

- Pyroxene:** a group of silicate minerals of the form $XY(Si,Al)_2O_6$. (where X is typically calcium, sodium, iron²⁺ and magnesium and Y represents smaller ions, such as aluminium, iron³⁺, magnesium and manganese).
- Pyroxferroite:** a **pyroxenoid** mineral rich in iron, $(Fe^{2+}Ca)SiO_3$.
- Pyroxenoid:** a mineral group structurally related to the pyroxens, with general formula $XSiO_3$, where X is a large-radius divalent cation, typically calcium, manganese or iron.
- Pyroxmangite:** a pyroxenoid mineral rich in manganese, $MnSiO_3$
- Quench:** to cool rapidly from high temperature.
- Rare earth element:** the lanthanide elements (atomic numbers 57-71), also sometimes includes yttrium and scandium.
- REE:** abbreviation for **rare earth elements**. Also LREE, MREE and HREE for the light, middle and heavy rare earth elements.
- Refinery:** the refinery process was an intermediate oxidative technique in **conversion**, to remove, by oxidation, many of the impurities in pig iron, so that **puddling** could remove the remainder. Pig iron (**typically grey cast iron**) was refined to **finers metal**, a **white cast iron**, and cast into thin plates.
- Reverberatory furnace:** a type of furnace in which heat was drawn from the firebox at one end of the furnace by the draught induced by a tall chimney at the other. In between the shape of the roof deflected and reflected heat onto the charge. They allowed the use of coal as fuel, without the coal coming into direct contact with the metal being heated. They were used in **puddling**, in reheating iron (including for joining small iron pieces together – balling), and also for melting iron in foundries.
- Run-out trough:** a thick cast iron trough, fitted over the top of a water-filled cistern, to quench **the finers metal** tapped from the **refinery**.
- Running-out furnace:** a refinery in which solid pig iron was melted, with the **finers metal** run-out into a **trough** at the conclusion of the reaction (as opposed to a running-in fire, in which liquid iron from the blast furnace flowed directly into the refinery).
- Sarcopside:** an iron, manganese and magnesium phosphate mineral: $(Fe^{2+}, Mn, Mg)_3(PO_4)_2$
- SEM:** scanning electron microscope.
- Semi-product:** a material formed during one stage of an industrial process (*chaîne opératoire*) which then forms the raw material for a subsequent stage.
- Sillimanite:** an alumino-silicate mineral, Al_2SiO_5 .
- Spheroidal hammerscale:** fine spheroidal slag (<2mm) produced by expulsion of a molten scale from iron during forging, particularly during fire welding.
- Spinel:** a mineral group with the general formula $X^{2+}Y^{3+}_2O_4$, which includes, amongst many others, the minerals **hercynite** and **magnetite**.
- Stamping:** crushing under mechanical stamps or hammers
- Steadite:** a eutectic of ferrite and iron phosphide (Fe_3P)
- Steel:** an alloy of iron with carbon with the carbon content being between 0.002% and 2.1% by weight.
- Stoichiometry:** the relative quantities of materials in a chemical reaction or formula.
- Tap slag (or tapped slag, sometimes tapslag):** slag that has been **tapped** from a furnace as a liquid to solidify outside the furnace.
- Tapping:** the process or act of allowing a liquid to flow from a furnace. In the bloomery process it is the slag that may be tapped; in a **blast furnace** both slag and iron are tapped.
- Trough:** see **run-out trough**.
- Tridymite:** a high temperature silica (SiO_2) polymorph.
- Tubular vesicle:** an elongate pore running vertically through a slag, caused by slag cooling around a rising stream of gas.
- Tuyère:** a tubular object for introducing the air blast into a hearth of furnace.
- Ulvospinel:** a titanium-bearing member of the spinel group of minerals, Fe_2TiO_4
- Valency:** a measure of the number of bonds formed by an atom of a given element
- Vesicle:** a void or pore, usually rounded and formed as a preserved gas bubble in a solidified melt.
- Wet puddling:** **puddling** using an iron bottom and **fettling** of iron oxide rich material to promote slag formation. In contrast, slag could not be retained on a sand-based **dry puddling** furnace because of the reaction with the sand.
- White cast iron:** a **cast iron** in which the carbon is present in iron carbide (as opposed to **grey cast iron**)
- Wrought iron:** a malleable composite material of low-carbon iron and slag, produced by decarburising pig iron.
- Wustite:** an iron II oxide FeO .
- XRF:** X-Ray Fluorescence; an analytical technique to identify elements by their characteristic X-Ray emissions when subject to an incident X-Ray beam.

Table 1: Details of samples selected for further analysis.

Sample	Source	Specimen notes	Category	SEM	Chem	Sampling notes
YSF1	u/s	lightweight, porous, clinker with shale clast	clinker	y	y	samples from dense part outer surface
YSF2	u/s	dense refinery slag with slightly lobed top; vesicles particularly in slightly lobate top and as tubes near base.	refinery	y	y	Chem = bulk section; SEM= near base
YSF3	u/s	dense refinery slag in two layers- lower dense with sparse tubular vesicles; upper highly vesicular, large tabular voids unroofed on top	refinery	y	y	from upper frothy layer
YSF4		same piece as 3	refinery	y	y	from lower dense layer
YSF5	c307 s145	block of vesicular refinery slag with ropey upper surface; recovered from in-situ flow in drain [236]	refinery	y	y	samples from just below smooth top
YSF6	u/s	large block of slag of very variable slag with abundant pale (sandstone?) clasts and coke lumps	Bessemer	y	y	samples from surface lobe
YSF7	u/s	large viscous flow lobe of slag, highly porous; somewhat brown internally, full of partially melted 'ceramic' clasts	Bessemer	y	y	samples from random position in lobe
YSF8	u/s	highly vesicular flow-lobate refinery slag.	refinery	y	y	samples from lower porous part, SEM includes base
YSF9	u/s	thin vesicular flow-lobate sheet of refinery slag, attached to a breccia of spheroids, fuel debris etc on base	refinery	y	y	from denser material below smooth surface
YSF10	u/s	dense, flat-topped refinery slag, dense body with tubular vesicles in places, overlain by porous flow lobed section in thin sheet.	refinery	y	y	Chem = bulk section; SEM near the base
YSF11	c377 s154	spheroids	micro	y	y	Additional sample 11a from <100µm fraction
YSF12	c122 s42	spheroids	micro	y	y	
YSF13	u/s	fragment of casting - or slab of semi-product; drawing 213 #2	iron	y		
YSF14	c179	cast iron runner fragment, irregular, drawing 39 #3	iron	y		
YSF15	c194	large pig or concavo-convex runner; has cavernous texture; drawing 47 #1	iron	y		
YSF16	c194	well-formed long pig tip, drawing 45 #7	iron	y		
YSF17	c126	runner of glassy blast furnace slag on iron - end of pig tapping	BF	y	y	slag
YSF18		same piece as 17	iron	y		iron from above
YSF19	u/s	flow of grey stony slag with glassy surface; iron, slag and fuel clasts on base	BF	y	y	
YSF20	u/s	flow of grey stony slag; central cavity; deeply glassy undulating top	BF		y	
YSF21	u/s	large block of somewhat weathered flowed grey stony slag	BF	y	y	samples from unweathered core,
YSF22	u/s	large block of somewhat weathered flowed pale grey stony slag	BF	y	y	from inner mid upper section
YSF23	c198	highly vesicular slag with iron clasts	BF	y	y	SEM covers join of frothy and dense basal layers
YSF24	u/s	highly vesicular slag with grey denser lower layer	BF	y	y	Chem. is frothy slag; SEM includes iron clast
YSF25	u/s	flat dense flowed slag, smooth top, dimpled base	refinery	y	y	whole section
YSF26	u/s	flat dense slag, smooth top, base has strange smooth skin, possible spheroids; passes into dense slag with tubular vesicles	refinery		y	whole section
YSF27	u/s	extremely dense slag, base curved; non wetted with hint of lobes on one side, becomes rougher on other; top wrinkled and rough	refinery	y	y	v pale grey coarsely crystalline slag from core
YSF28	u/s	curved slag sheet, base finely fuel dimpled with adhering slag fragments	refinery		y	whole section
YSF29	c305	thin slag sheet, smooth with fine dimples on base, slag highly vesicular, top obscured by rusty concretion but appears rough in detail although planar	refinery	y	y	whole section
YSF30	u/s	extremely dense slag with roughly right angle curved base, base and side are non-wetted with lobes	refinery/ puddling	y	y	chilled zone, coarse, just above base
YSF31		same piece as 30		y	y	zone with small vesicles just below large vesicles at top
YSF32	u/s	extremely dense slag in thick sheet, then abrupt change to upper section with large tabular vesicles and upper flow-lobed texture	refinery		y	complete section

Table 2: Major element analyses of samples by XRF, expressed in oxide wt%. LOI = loss on ignition. Iron expressed alternatively as Fe₂O₃ or FeO

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Mn ₃ O ₄	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃	LOI	Total
clinker														
YSF1	56.02	23.59	10.63	9.57	0.19	1.83	0.25	0.33	5.25	1.03	0.150	0.088	-0.82	99.68
refinery slags														
YSF2	15.87	4.01	69.35	62.42	2.63	0.28	0.60	0.08	0.25	0.51	5.563	0.272	-4.46	101.13
YSF3	16.13	3.66	69.31	62.38	2.76	0.27	0.55	0.10	0.27	0.47	5.544	0.333	-6.52	100.74
YSF4	15.84	3.72	68.64	61.78	2.71	0.29	0.60	0.10	0.29	0.47	5.722	0.314	-6.66	99.93
YSF5	11.72	2.55	78.73	70.86	1.17	0.15	0.16	0.01	0.02	0.28	3.480	0.523	-4.85	99.70
YSF8	12.91	2.68	71.02	63.92	4.63	0.38	0.49	0.05	0.07	0.38	6.458	0.803	-2.71	101.46
YSF9	12.33	2.09	74.20	66.78	2.45	0.20	1.01	0.05	0.09	0.37	6.872	0.432	-5.06	101.15
YSF10	16.78	4.14	67.41	60.67	2.77	0.33	0.59	0.09	0.31	0.51	4.848	0.143	-5.99	99.36
YSF25	16.01	3.83	68.93	62.03	2.72	0.27	0.60	0.13	0.31	0.54	5.133	0.225	-6.60	100.31
YSF26	16.01	3.93	70.33	63.30	2.73	0.28	0.56	0.09	0.30	0.55	5.050	0.190	-6.61	101.67
YSF27	16.63	4.05	67.95	61.16	2.78	0.33	0.58	0.10	0.30	0.53	5.030	0.142	-6.69	99.84
YSF28	16.76	4.45	66.47	59.82	2.56	0.66	2.00	0.11	0.36	0.54	4.710	0.253	-6.19	100.58
YSF29	12.87	3.00	76.32	68.68	1.81	0.24	0.47	0.04	0.16	0.41	5.178	0.586	-3.90	102.52
YSF32	15.78	3.96	70.61	63.55	2.72	0.28	0.54	0.09	0.27	0.51	5.540	0.325	-6.43	102.31
refinery/puddling slags														
YSF30	16.47	1.11	72.97	65.67	2.45	0.09	0.17	0.03	0.07	0.42	4.118	0.851	-6.10	100.30
YSF31	16.83	0.82	73.88	66.49	2.45	0.02	0.18	0.02	0.08	0.42	4.116	0.868	-6.45	101.20
refinery spheroids														
YSF11	11.93	2.58	79.38	71.44	1.24	0.24	0.52	0.04	0.20	0.31	2.702	0.077	1.28	101.19
YSF12	15.27	2.95	72.09	64.88	1.09	0.29	0.86	0.07	0.28	0.35	2.767	0.284	3.42	100.56
acid Bessemer slags														
YSF6	54.14	2.07	22.59	20.33	18.76	0.05	<0.004	0.01	0.29	0.99	0.067	0.140	-2.85	100.75
YSF7	57.84	1.62	26.16	23.55	12.28	0.05	<0.004	0.00	0.22	0.97	0.018	0.205	-2.28	100.48
blast furnace slags														
YSF17	37.04	11.01	12.84	11.55	1.81	2.12	31.84	0.37	1.60	0.61	0.425	0.500	-3.02	101.07
YSF19	35.40	14.32	0.33	0.30	1.20	9.58	34.17	0.48	1.92	0.72	0.008	0.216	-0.61	98.87
YSF20	35.31	14.23	0.80	0.72	1.20	9.47	34.37	0.52	1.73	0.69	0.025	0.637	-1.31	99.92
YSF21	37.23	15.48	2.78	2.50	1.37	9.96	28.28	0.45	2.28	0.70	0.067	0.284	-0.62	99.53
YSF22	35.78	14.99	0.66	0.59	0.88	9.37	32.10	0.42	1.79	0.60	0.004	0.195	2.23	99.53
YSF23	37.00	15.56	1.09	0.98	1.34	10.24	29.62	0.46	2.30	0.71	0.031	0.199	-0.34	99.11
YSF24	33.11	15.05	2.29	2.06	1.12	8.28	35.69	0.37	1.47	0.54	0.120	0.116	-0.39	98.60

Table 3a: Trace elements analysed by ICP-MS, expressed in ppm.

	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Mo	Sn	Cs	Ba
<i>clinker</i>																	
YSF1	23.9	226.4	173.5	56.2	55.4	227.3	124.9	12.6	211.5	259.9	42.8	213.3	21.52	3.96	3.18	13.19	735.7
<i>refinery slag</i>																	
YSF2	6.2	4639.7	1934.8	376.4	8.6	389.8	88.2	43.2	9.2	250.2	11.4	94.8	116.54	0.77	1.50	0.51	289.1
YSF3	6.1	3193.1	956.5	395.9	12.5	484.2	111.9	41.0	10.2	236.7	11.4	95.9	124.72	0.81	0.67	0.53	287.3
YSF4	6.1	2908.5	784.3	394.9	108.6	410.5	81.8	40.9	11.0	254.4	12.3	102.9	138.01	0.83	1.34	0.54	312.3
YSF5	5.0	803.6	535.0	456.0	14.4	350.8	79.2	50.7	2.0	104.0	8.2	93.7	58.80	1.11	2.50	0.23	296.8
YSF8	3.2	670.7	291.7	208.8	7.4	298.7	78.5	30.6	1.7	158.0	5.6	49.6	36.99	1.00	1.54	0.30	275.2
YSF9	4.3	1186.7	767.6	422.7	202.5	403.3	84.0	57.6	3.5	258.0	8.9	78.6	66.76	1.09	3.23	0.27	383.6
YSF10	6.6	4650.2	1880.9	289.3	107.0	17.8	3.7	37.9	13.3	245.5	12.3	96.6	111.31	1.30	2.69	0.79	326.9
YSF25	6.6	4985.6	2212.2	195.5	69.3	50.1	7.5	40.2	13.0	244.1	12.1	80.2	93.76	1.04	2.45	0.75	322.3
YSF26	5.0	4864.7	2028.1	330.9	16.1	213.1	52.6	40.7	12.9	224.1	11.1	88.6	103.80	1.52	3.31	0.67	299.70
YSF27	5.5	3589.2	1374.0	346.4	9.2	328.1	59.8	40.5	11.4	323.4	10.8	104.3	115.74	1.23	3.93	0.55	290.8
YSF28	6.3	5092.3	2247.2	404.8	5.6	411.1	79.3	37.7	11.5	340.5	11.5	93.3	114.60	1.61	2.44	0.54	309.5
YSF29	5.6	3019.5	1262.1	505.2	89.6	534.2	115.2	42.1	11.4	219.6	10.9	101.4	101.98	1.32	2.12	0.58	279.8
YSF32	6.7	5096.0	2157.0	178.5	12.6	24.7	24.3	40.3	10.7	231.5	12.5	125.5	119.30	1.57	0.50	0.35	295.5
<i>refinery/puddling slag</i>																	
YSF30	1.4	1969.0	798.3	447.6	6.3	486.7	162.4	41.8	5.6	91.4	2.4	71.5	91.07	1.28	9.44	0.31	206.5
YSF31	2.1	1805.2	588.3	449.8	3.4	623.4	196.7	29.8	3.3	90.5	2.1	79.0	43.08	1.46	6.21	0.22	172.3
<i>refinery spheroids</i>																	
YSF11	4.1	1354.5	665.0	433.1	37.4	468.8	108.2	33.2	7.4	202.1	8.0	77.8	61.99	5.81	3.72	0.50	270.7
YSF12	6.7	1294.6	789.2	403.5	39.3	1327.6	480.5	33.3	13.0	247.3	10.6	100.9	64.34	6.54	3.46	0.94	423.2
<i>acid Bessemer slags</i>																	
YSF6	2.7	538.6	233.1	93.3	662.5	31.6	6.3	16.4	13.8	29.7	3.9	105.4	37.02	0.77	2.51	1.28	125.2
YSF7	1.0	225.6	65.1	96.2	6.4	212.0	41.1	13.3	6.5	13.0	2.1	65.5	19.31	2.04	1.48	0.53	44.9
<i>blast furnace slags</i>																	
YSF17	16.8	335.0	162.6	68.8	31.4	24.4	30.3	6.5	68.7	653.9	75.3	276.6	14.15	1.85	0.33	4.74	636.1
YSF19	35.0	43.9	15.1	5.5	35.7	237.8	70.7	4.1	57.5	790.5	76.8	246.0	6.54	0.68	0.80	2.12	1122.8
YSF20	33.9	32.0	31.4	45.3	36.1	1.8	7.5	2.2	65.2	692.8	70.2	208.5	5.64	0.24	2.22	3.08	1217.6
YSF21	41.7	29.7	10.0	3.3	2.6	179.2	46.8	3.2	57.3	734.4	81.5	214.4	2.03	-0.04	0.55	1.85	1216.1
YSF22	38.1	97.7	8.4	15.0	2.5	345.2	98.6	8.0	41.7	1391.6	90.5	182.1	6.49	3.43	1.66	1.48	255.8
YSF23	46.5	84.4	1193.5	9.5	887.9	180.5	78.0	5.1	82.6	953.0	94.1	199.0	6.53	1.09	3.74	3.30	1413.0
YSF24	23.9	44.6	5.6	8.2	4.6	88.1	23.7	2.5	27.1	503.5	52.5	102.7	5.44	0.28	0.82	1.12	758.3

Table 3b: Trace elements analysed by ICP-MS, expressed in ppm. (contd.)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
clinker																			
YSF1	57.78	110.79	14.09	50.70	9.84	2.30	8.52	1.17	7.06	1.23	3.72	0.60	3.67	0.59	5.22	1.75	9.22	16.90	4.63
refinery slag																			
YSF2	13.15	23.63	3.02	11.46	2.35	0.65	2.02	0.36	2.03	0.33	0.94	0.15	0.91	0.15	2.26	3.42	4.25	3.46	0.88
YSF3	13.17	23.92	3.08	11.54	2.26	0.67	2.03	0.37	2.05	0.34	0.96	0.16	0.94	0.14	2.21	4.06	3.50	3.46	0.95
YSF4	14.31	26.02	3.34	12.69	2.35	0.70	2.15	0.39	2.16	0.37	1.04	0.16	1.01	0.15	2.43	3.66	3.72	3.63	1.00
YSF5	8.28	15.37	2.01	7.36	1.55	0.49	1.15	0.24	1.39	0.25	0.71	0.12	0.67	0.10	2.11	2.52	4.22	2.22	0.76
YSF8	4.79	8.83	1.18	4.80	1.22	0.40	0.88	0.18	1.09	0.19	0.47	0.08	0.45	0.06	1.10	1.66	2.30	1.14	0.34
YSF9	7.93	14.62	1.94	7.33	1.60	0.54	1.45	0.27	1.53	0.27	0.68	0.13	0.62	0.08	1.79	2.79	2.92	1.81	0.59
YSF10	14.26	26.89	3.23	11.52	2.42	0.63	2.55	0.34	1.92	0.34	0.99	0.15	0.91	0.13	2.40	3.27	5.44	2.99	0.89
YSF25	13.61	26.19	3.13	11.56	2.48	0.64	2.37	0.30	1.92	0.34	1.03	0.14	0.85	0.13	2.15	5.14	9.84	3.21	0.87
YSF26	13.56	25.66	3.10	11.07	2.32	0.65	2.50	0.35	2.11	0.36	1.02	0.16	0.95	0.13	2.39	3.47	3.72	2.97	0.79
YSF27	13.27	24.45	3.17	11.47	2.46	0.63	2.04	0.36	2.13	0.35	0.94	0.15	0.93	0.13	2.27	3.53	3.04	2.62	1.00
YSF28	13.85	25.22	3.26	11.41	2.47	0.66	2.08	0.35	2.23	0.37	0.97	0.16	0.88	0.13	2.76	3.77	4.24	2.10	0.91
YSF29	12.89	23.74	3.04	10.92	2.44	0.62	1.89	0.36	2.00	0.34	0.91	0.15	0.93	0.12	2.11	3.36	4.16	1.83	0.87
YSF32	14.21	26.29	3.16	12.11	2.46	0.61	2.29	0.37	1.93	0.38	1.06	0.16	1.01	0.14	2.41	4.74	3.27	3.35	0.95
refinery/puddling slag																			
YSF30	9.81	18.29	2.37	8.66	1.85	0.51	1.49	0.27	1.61	0.28	0.79	0.13	0.71	0.11	1.84	3.32	19.91	2.58	0.83
YSF31	3.53	6.00	0.71	2.54	0.52	0.20	0.51	0.08	0.39	0.07	0.24	0.04	0.26	0.03	1.57	2.61	209.90	0.81	0.62
refinery spheroids																			
YSF11	7.81	14.21	1.87	7.13	1.61	0.48	1.24	0.25	1.33	0.26	0.61	0.10	0.58	0.07	2.01	2.19	284.59	1.93	0.82
YSF12	10.09	18.90	2.45	9.13	2.11	0.68	1.69	0.34	1.81	0.32	0.89	0.14	0.84	0.12	2.15	2.41	19.12	3.26	0.99
acid Bessemer slags																			
YSF6	6.24	11.92	1.38	4.37	0.88	0.23	0.79	0.10	0.68	0.13	0.42	0.06	0.42	0.06	2.35	3.69	7.94	1.57	0.56
YSF7	3.13	5.83	0.70	2.39	0.51	0.12	0.34	0.08	0.39	0.07	0.23	0.03	0.21	0.03	1.55	2.20	4.60	0.86	0.40
blast furnace slags																			
YSF17	47.51	103.70	13.10	52.36	11.74	2.87	12.23	1.90	11.10	2.21	6.45	1.02	6.29	0.90	5.19	1.35	1.81	13.51	5.03
YSF19	45.32	88.42	11.59	44.00	9.80	3.19	11.85	1.76	10.94	1.96	5.19	0.83	4.88	0.67	5.32	1.91	4.84	10.11	4.40
YSF20	47.47	96.30	11.76	45.76	10.48	2.96	12.07	1.86	10.62	1.76	5.29	0.69	4.55	0.62	5.41	1.59	3.73	9.09	3.69
YSF21	44.98	89.73	12.02	44.93	10.93	3.45	12.78	1.99	13.05	2.15	5.68	0.87	5.04	0.78	4.85	0.88	2.00	6.14	5.03
YSF22	16.50	33.07	4.06	14.26	2.81	0.61	2.10	0.42	2.75	0.47	1.41	0.25	1.59	0.25	5.70	1.75	16.82	3.65	1.61
YSF23	50.72	101.25	13.79	52.31	13.07	4.16	16.17	2.48	15.53	2.59	6.79	1.01	5.94	0.89	4.68	1.05	4.05	6.78	5.71
YSF24	28.72	54.33	7.65	29.21	7.32	2.47	8.57	1.36	8.25	1.34	3.51	0.53	2.90	0.47	2.46	3.02	1.91	3.19	4.49

Table 4: EDS Micro-analyses of the constituent minerals of blast furnace slags.

EDS Analysis (normalised atom %)														Mineral formula												
S	SOI	#	O	Na	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	O	Na	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe		
Al-enstatite																										
23	7	7	59.74	0.17	7.52	9.54	14.30	0.16	1.38	6.31	0.49	0.28	0.11	6	0.02	0.76	0.96	1.44	0.02	0.14	0.63	0.05	0.03	0.01		
22	8	8	58.89	0.48	6.16	10.19	14.52	0.28	3.27	5.20	0.62	0.38		6	0.05	0.63	1.04	1.48	0.03	0.33	0.53	0.06	0.04			
22	8	9	59.64	0.22	7.03	9.27	14.38	0.22	1.48	7.02	0.49	0.26		6	0.02	0.71	0.93	1.45	0.02	0.15	0.71	0.05	0.03			
23	2	1	60.02		7.77	8.77	14.14	0.40	1.57	6.24	0.45	0.41	0.22	6		0.78	0.88	1.41	0.04	0.16	0.62	0.04	0.04	0.02		
21	5	7	57.72		6.91	8.98	15.38	0.47	0.99	8.88	0.43	0.24		6		0.72	0.93	1.6	0.05	0.1	0.92	0.04	0.03			
21	5	8	57.46	<	6.50	9.48	15.32	0.50	0.43	9.60	0.44	0.27		6		0.68	0.99	1.6	0.05	0.04	1	0.05	0.03			
21	5	9	57.98		6.56	9.17	15.38	0.31	0.36	9.59	0.52	0.15		6		0.68	0.95	1.59	0.03	0.04	0.99	0.05	0.02			
21	5	10	58.22		7.85	9.24	14.59			8.82	1.28			6		0.81	0.95	1.5			0.91	0.13				
Fassaite																										
17	9	5	59.70	0.53	1.98	6.65	15.83	0.20	0.95	12.66	0.22	0.72	0.56	6	0.05	0.2	0.67	1.59	0.02	0.1	1.27	0.02	0.07	0.06		
17	6	7	59.53	0.62	1.99	7.19	14.75	0.18	0.75	13.70	0.13	0.65	0.49	6	0.06	0.2	0.72	1.49	0.02	0.08	1.38	0.01	0.07	0.05		
17	6	8	59.38	0.60	2.11	7.61	14.60	0.14	0.69	13.74	0.14	0.53	0.46	6	0.06	0.21	0.77	1.48	0.01	0.07	1.39	0.01	0.05	0.05		
17	9	11	60.01	0.49	2.34	6.30	14.88	0.26	0.72	13.61	0.18	0.63	0.58	6	0.05	0.23	0.63	1.49	0.03	0.07	1.36	0.02	0.06	0.06		
17	9	1	59.54	0.50	2.39	6.47	14.92	0.22	0.77	13.77	0.18	0.64	0.61	6	0.05	0.24	0.65	1.5	0.02	0.08	1.39	0.02	0.06	0.06		
17	6	5	59.09	0.66	2.88	6.79	14.43	0.07	0.37	14.91	0.08	0.46	0.27	6	0.07	0.29	0.69	1.46	0.01	0.04	1.51	0.01	0.05	0.03		
17	6	6	59.80	0.69	3.08	6.34	14.43	0.05	0.37	14.52	0.05	0.35	0.32	6	0.07	0.31	0.64	1.45	0.01	0.04	1.46	0.01	0.04	0.03		
Melilite																										
19	5	1	60%	57.78	0.30	4.83	6.40	13.83		0.17	16.71			14	0.07	1.17	1.55	3.35		0.04	4.05					
19	5	2	61%	58.11	0.58	4.87	6.14	13.91		0.19	16.19			14	0.14	1.17	1.48	3.35		0.05	3.9					
19	5	4	63%	58.09	0.36	5.06	5.86	13.94		0.21	16.47			14	0.09	1.22	1.41	3.36		0.05	3.97					
21	5	5	61%	57.21	0.42	4.90	6.19	14.22		0.21	16.78	0.08		14	0.1	1.2	1.52	3.48		0.05	4.11		0.02			
21	5	4	61%	57.13	0.44	4.92	6.17	14.34	<	0.32	16.68			14	0.11	1.21	1.51	3.51		0.08	4.09					
21	5	1	63%	57.24	0.49	5.09	6.10	14.09		0.18	16.81			14	0.12	1.25	1.49	3.45		0.04	4.11					
21	5	2	65%	57.10	0.56	5.12	5.63	14.51	0.06	0.25	16.67	0.11		14	0.14	1.26	1.38	3.56	0.01	0.06	4.09		0.03			
21	5	3	67%	57.09	0.58	5.36	5.28	14.73	<	0.30	16.65			14	0.14	1.32	1.3	3.61		0.07	4.08					
22	8	3	60%	58.86	0.51	4.60	6.08	13.80		0.37	15.71	0.07		14	0.12	1.1	1.45	3.28		0.09	3.74		0.02			
22	8	2	61%	58.52	0.63	4.80	6.01	13.92		0.38	15.69	0.05		14	0.15	1.15	1.44	3.33		0.09	3.75		0.01			
22	8	4	64%	58.60	0.49	5.01	5.61	14.08		0.32	15.80	0.08		14	0.12	1.2	1.34	3.36		0.08	3.77		0.02			
22	8	1	64%	58.58	0.54	5.03	5.63	14.03		0.39	15.72	0.07		14	0.13	1.2	1.35	3.35		0.09	3.76		0.02			
23	7	5	60%	59.09	0.53	4.54	6.06	14.01		0.38	15.34	0.06		14	0.13	1.08	1.44	3.32		0.09	3.63		0.01			
23	2	3	59%	58.62	0.58	4.55	6.36	14.15	0.20	0.46	14.66	0.13	0.09	14	0.14	1.09	1.52	3.38	0.05	0.11	3.5	0.03	0.05	0.02		
23	2	2	59%	58.65	0.56	4.58	6.39	14.07	0.23	0.50	14.60	0.09	0.10	14	0.13	1.09	1.53	3.36	0.05	0.12	3.48	0.02	0.05	0.02		
Pseudowollastonite																										
17	6	1		61.22	<	0.35	0.73	18.86	<	0.10	18.33	0.08	0.22	3		0.02	0.04	0.92		0	0.9	0	0.01	0.01		
17	6	3		61.19		0.33	0.52	18.81			18.71	0.08	0.18	3		0.02	0.03	0.92			0.92	0	0.01	0.01		
17	9	3		61.06		0.33	0.51	18.84	<		18.87	0.08	0.18	3		0.02	0.02	0.93			0.93	0	0.01	0.01		
17	6	2		59.26	0.15	0.62	4.96	17.94	0.17	0.99	14.76	0.23	0.46	3	0.01	0.03	0.25	0.91	0.01	0.05	0.75	0.01	0.02	0.02		
17	9	2		61.31	<	0.50	1.12	18.26			18.32	0.09	0.27	3		0.02	0.05	0.89			0.9	0	0.01	0.01		
17	9	4		61.11		0.44	0.94	18.65		0.11	18.23	0.10	0.24	3		0.02	0.05	0.92		0.01	0.89	0	0.01	0.01		

Table 5: Major element chemical composition of BF slags

			Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Mn ₃ O ₄	FeO
YSF17		XRF	0.37	2.14	11.14	37.46	0.43	0.51	1.62	32.20	0.62	1.83	11.68
SOI2	#1	EDS	0.49	2.34	12.61	41.84	<	0.95	1.69	34.22	0.67	1.70	2.39
SOI3	#1	EDS	0.47	2.16	12.42	40.85	0.25	0.94	1.65	33.56	0.71	1.78	2.65
SOI4	#1	EDS	0.40	2.18	12.46	41.05	<	0.76	1.58	33.02	0.63	1.78	2.79
SOI5	#1	EDS	0.43	2.30	12.47	41.17	0.19	0.69	1.61	33.63	0.64	1.74	2.48
SOI7	#1	EDS	0.54	2.33	11.93	39.78	0.22	0.76	1.61	31.95	0.63	1.72	2.72
		average	0.46	2.26	12.38	40.94	0.13	0.82	1.63	33.28	0.65	1.74	2.60
YSF19		XRF	0.49	9.74	14.57	36.01	0.01	0.22	1.95	34.76	0.73	1.22	0.31
SOI1	#1	EDS	0.45	8.89	14.19	35.47	<	0.66	1.48	36.34	0.78	0.97	<
SOI2	#1	EDS	0.53	9.14	14.51	35.37	<	0.68	1.54	36.18	0.74	1.27	0.19
SOI3	#1	EDS	0.51	8.98	14.46	35.67	<	0.61	1.38	36.86	0.70	1.16	<
SOI4	#1	EDS	0.38	9.22	14.16	36.21	<	0.70	1.49	36.11	0.72	1.08	<
SOI6	#1	EDS	0.51	9.73	14.68	36.81	<	0.74	1.65	34.89	0.75	1.30	<
		average	0.48	9.19	14.40	35.91	<	0.68	1.51	36.08	0.74	1.15	0.04
YSF20		XRF	0.53	9.58	14.39	35.70	0.03	0.64	1.75	34.75	0.70	1.21	0.73
YSF21		XRF	0.46	10.10	15.70	37.76	0.07	0.29	2.31	28.68	0.71	1.39	2.54
SOI2	#1	EDS	0.56	9.08	15.79	38.53	<	0.73	2.05	33.45	0.55	0.94	<
SOI3	#1	EDS	0.53	9.41	16.28	38.39	<	0.75	2.11	32.85	0.83	0.93	<
SOI4	#1	EDS	0.50	9.36	15.68	38.30	<	0.73	1.95	33.50	0.69	0.93	0.30
		average	0.53	9.28	15.91	38.41	<	0.74	2.04	33.27	0.69	0.93	0.10
YSF22		XRF	0.43	9.69	15.50	36.99	<	0.20	1.85	33.19	0.62	0.91	0.61
SOI1	#1	EDS	0.65	8.77	15.78	35.29	<	0.65	2.44	31.04	0.76	1.23	0.33
SOI2	#1	EDS	0.61	8.79	16.15	36.32	<	0.66	2.46	31.13	0.58	1.28	0.49
SOI3	#1	EDS	0.71	8.76	16.05	36.18	<	0.56	2.43	31.92	0.58	1.17	0.31
SOI4	#1	EDS	0.59	9.18	16.33	36.31	<	0.59	2.56	31.03	0.69	1.26	0.30
SOI5	#1	EDS	0.60	8.04	16.28	35.24	<	0.16	1.91	31.00	0.79	1.42	0.79
SOI6	#1	EDS	0.61	8.99	16.34	36.28	<	0.63	2.68	29.88	0.74	1.34	0.79
		average	0.63	8.75	16.16	35.94	<	0.54	2.41	31.00	0.69	1.28	0.50
YSF23		XRF	0.47	10.40	15.81	37.59	0.03	0.20	2.34	30.09	0.72	1.36	1.00
SOI1	#1	EDS	0.56	9.90	16.18	38.55	<	0.65	2.21	28.31	0.61	1.32	0.64
SOI3	#1	EDS	0.50	9.74	16.19	38.32	<	0.61	2.28	28.10	0.81	1.34	0.64
SOI4	#1	EDS	0.55	9.94	16.30	37.85	<	0.64	2.26	27.66	0.82	1.37	0.64
SOI5	#1	EDS	0.55	9.93	16.32	37.97	<	0.57	2.24	28.21	0.69	1.21	0.68
SOI6	#1	EDS	0.42	9.92	16.06	38.13	<	0.59	2.24	28.06	0.78	1.35	0.67
		average	0.52	9.89	16.21	38.16	<	0.61	2.25	28.07	0.74	1.32	0.65
YSF24		XRF	0.38	8.46	15.37	33.81	0.12	0.12	1.50	36.45	0.55	1.14	2.10

Table 6: Major element chemical composition of cast irons (normalised to 100% excluding carbon)

wt%	Si	P	S	Ti	V	Mn	Fe
YSF13	0.83	0.87	0.33			0.66	97.25
YSF14	2.33	0.80	0.82			0.14	95.91
YSF15	2.61	<	<	<		0.80	96.41
YSF16	2.38	<	<	<		1.10	96.37
YSF18	1.38	1.26	5.14	0.14	<	6.81	85.24
YSF24	1.24	0.94	0.26			0.89	96.66

Table 7: Typical compositions of pig iron, in wt%, after Forsythe (1908, p. 287)

Grade of iron	Si	S	P	Mn
No. 1 foundry	2.5-3.0	<.035	0.5-1.0	<3.0
No. 2 foundry	2.0-2.5	<.045	0.5-1.0	<1.0
No. 3 foundry	1.5-2.0	<.053	0.5-1.0	<1.0
Malleable	0.75-1.50	<.050	<0.2	<1.0
Gray forge	<1.50	<0.1	<1.0	<1.0
Bessemer	1.0-2.0	<0.05	<0.1	<1.0
Low phosphorus	<2.0	<0.03	<0.03	<1.0
Basic	<1.0	<.05	<1.0	<1.0
Thomas Gilchrist or basic Bessemer	<1.0	<0.05	2.0-3.0	1.0-2.0

Table 8: Major element chemical composition of refining slags

		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO
YSF2	XRF	0.09	0.30	4.28	16.95	5.94	0.29	0.27	0.64	0.54	0.92	0.33	2.81	66.65
	EDS	0.27	0.40	4.66	18.35	6.37	0.13	0.33	0.69	0.44	1.09	0.37	2.97	64.66
YSF3	XRF	0.11	0.29	3.93	17.31	5.95	0.36	0.29	0.59	0.50	0.61	0.16	2.96	66.95
	EDS	0.32	0.33	4.23	18.08	7.79	0.24	0.42	0.92	0.43	0.67	<	2.98	65.66
YSF4	XRF	0.11	0.31	4.02	17.13	6.19	0.34	0.31	0.65	0.51	0.54	0.13	2.93	66.82
	EDS	0.34	0.37	4.19	19.40	6.95	0.16	0.32	0.78	0.38	0.45	<	3.09	66.66
YSF5	XRF	0.01	0.16	2.80	12.86	3.82	0.57	0.02	0.18	0.31	0.14	0.08	1.28	77.76
	EDS	<	0.36	4.05	18.38	5.09	0.20	0.08	0.51	0.26	<	<	1.53	69.13
YSF8	XRF	0.05	0.41	2.88	13.87	6.94	0.86	0.08	0.53	0.41	0.25	0.10	4.97	68.66
	EDS	<	0.51	2.66	18.69	11.85	0.55	0.36	0.93	0.40	0.35	<	5.74	62.85
YSF9	XRF	0.05	0.21	2.25	13.25	7.39	0.46	0.10	1.09	0.40	0.23	0.15	2.63	71.79
	EDS	<	0.32	2.25	14.14	11.80	0.34	0.19	1.61	0.31	0.28	<	2.94	66.69
YSF10	XRF	0.10	0.36	4.49	18.21	5.26	0.16	0.34	0.64	0.55	0.79	0.29	3.01	65.82
	EDS	<	0.32	4.36	18.78	6.64	0.12	0.38	0.91	0.44	0.76	<	3.11	64.83
YSF25	XRF	0.14	0.29	4.12	17.23	5.53	0.24	0.33	0.65	0.58	0.84	0.34	2.93	66.77
	EDS	<	0.42	4.09	19.15	7.62	0.16	0.43	0.94	0.42	0.57	0.28	3.04	64.08
YSF26	XRF	0.10	0.30	4.17	17.00	5.36	0.20	0.32	0.59	0.58	0.89	0.36	2.90	67.22
YSF27	XRF	0.11	0.36	4.37	17.96	5.43	0.15	0.32	0.63	0.57	0.76	0.27	3.00	66.06
	EDS	<	0.37	4.36	19.27	6.95	0.11	0.38	0.85	0.45	0.65	0.31	3.08	63.67
YSF28	XRF	0.12	0.71	4.76	17.94	5.04	0.27	0.39	2.14	0.58	0.89	0.37	2.74	64.05
YSF29		0.04	0.26	3.19	13.68	5.50	0.62	0.17	0.50	0.44	0.47	0.18	1.92	73.02
	EDS	<	0.31	3.14	16.50	6.29	0.20	0.20	0.66	0.36	0.45	<	2.16	69.89
YSF32	XRF	0.10	0.30	4.18	16.67	5.85	0.34	0.29	0.57	0.54	0.85	0.31	2.87	67.13

Table 9: EDS Micro-analyses of the constituent minerals of refining slags (1): phosphoran fayalite.

Sample	Area	Point	EDS in atomic%									formula (4 oxygens)						
			O	Na	Mg	Al	Si	P	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al
YSF27	SOI11	#2	57.88		0.79	0.29	13.33	0.52	0.06	1.55	25.57	0.92	0.04	0.05	<	0.11	1.77	0.02
YSF27	SOI11	#3	56.08		0.52	0.31	13.23	0.51		1.63	27.72	0.94	0.04	0.04	<	0.12	1.98	0.02
YSF4	SOI 5	#7	55.02		0.39	0.39	14.10	0.55	<	1.36	28.20	1.03	0.04	0.03	<	0.10	2.05	0.03
YSF2	SOI9	#10	56.97		0.61	0.28	13.16	0.69	<	1.55	26.73	0.92	0.05	0.04	<	0.11	1.88	0.02
YSF5	SOI 2	#3	57.03	<	0.38	0.40	13.30	0.70	0.09	0.81	27.30	0.93	0.05	0.03	0.01	0.06	1.91	0.03
YSF2	SOI9	#9	56.76	<	0.46	0.35	13.20	0.74		1.50	26.99	0.93	0.05	0.03	<	0.11	1.90	0.02
YSF2	SOI9	#7	56.76	0.28	0.38	0.35	12.93	0.76	0.08	1.56	26.89	0.91	0.05	0.03	0.01	0.11	1.89	0.02
YSF10	SOI3	#6	57.26		0.35	0.36	13.10	0.79	<	1.53	26.61	0.92	0.06	0.02	<	0.11	1.86	0.03
YSF10	SOI3	#5	56.72		0.53	0.41	13.07	0.81		1.62	26.84	0.92	0.06	0.04	<	0.11	1.89	0.03
YSF27	SOI11	#1	57.55		0.78	0.34	13.02	0.83		1.67	25.80	0.91	0.06	0.05	<	0.12	1.79	0.02
YSF5	SOI 2	#4	56.96		0.30	0.39	13.12	0.86	0.06	0.79	27.51	0.92	0.06	0.02	<	0.06	1.93	0.03
YSF27	SOI11	#4	57.97	<	<	0.28	12.95	0.87		1.49	26.44	0.89	0.06	<	<	0.10	1.82	0.02
YSF27	SOI12	#6	57.66		0.45	0.41	13.08	0.93		1.44	26.03	0.91	0.06	0.03	<	0.10	1.81	0.03
YSF25	SOI2	#14	56.14	<	0.53	0.49	13.32	0.90	<	1.46	27.16	0.95	0.06	0.04	<	0.10	1.94	0.04
YSF2	SOI10	#17	57.34		0.40	0.40	13.06	0.93		1.39	26.47	0.91	0.07	0.03	<	0.10	1.85	0.03
YSF27	SOI11	#13	58.08	<	<	0.29	12.84	0.95	0.12	1.36	26.35	0.88	0.07	<	0.01	0.09	1.81	0.02
YSF3	SOI10	#3	54.53	<	0.58	0.39	14.04	0.90		1.52	28.04	1.03	0.07	0.04	<	0.11	2.06	0.03
YSF2	SOI7	#13	56.58		0.49	0.35	13.06	0.94		1.52	27.07	0.92	0.07	0.03	<	0.11	1.91	0.02
YSF10	SOI4	#5	56.98		0.47	0.47	12.95	0.94		1.55	26.64	0.91	0.07	0.03	<	0.11	1.87	0.03
YSF4	SOI 9	#13	55.63		0.55	0.36	13.46	0.93		1.60	27.47	0.97	0.07	0.04	<	0.12	1.98	0.03
YSF2	SOI7	#12	56.73	<	0.34	0.32	13.16	0.97		1.50	26.98	0.93	0.07	0.02	<	0.11	1.90	0.02
YSF2	SOI9	#11	57.21	<	0.73	0.31	12.77	0.98		1.59	26.41	0.89	0.07	0.05	<	0.11	1.85	0.02
YSF25	SOI1	#8	57.17		0.45	0.41	13.06	0.99		1.45	26.48	0.91	0.07	0.03	<	0.10	1.85	0.03
YSF4	SOI 9	#10	55.72		0.33	0.38	13.40	0.98		1.53	27.65	0.96	0.07	0.02	<	0.11	1.98	0.03
YSF10	SOI3	#7	56.96		0.24	0.28	12.85	1.01	0.08	1.56	27.03	0.90	0.07	0.02	0.01	0.11	1.90	0.02
YSF25	SOI4	#8	57.17	<	0.28	0.44	13.01	1.02	<	1.43	26.65	0.91	0.07	0.02	<	0.10	1.86	0.03
YSF25	SOI2	#13	56.68		0.16	0.30	13.29	1.03	0.09	1.15	27.31	0.94	0.07	0.01	0.01	0.08	1.93	0.02
YSF4	SOI 2	#7	54.94		0.33	0.43	13.62	1.01	0.09	1.53	28.05	0.99	0.07	0.02	0.01	0.11	2.04	0.03
YSF5	SOI 5	#1	56.96	<	0.31	0.44	12.95	1.05	0.06	0.84	27.38	0.91	0.07	0.02	<	0.06	1.92	0.03
YSF2	SOI10	#18	56.97	<	0.40	0.45	12.82	1.09		1.51	26.76	0.90	0.08	0.03	<	0.11	1.88	0.03
YSF27	SOI13	#14	58.19		0.46	0.32	12.81	1.12		2.37	24.73	0.88	0.08	0.03	<	0.16	1.70	0.02
YSF25	SOI4	#19	57.23		0.23	0.40	12.87	1.12	<	1.30	26.84	0.90	0.08	0.02	<	0.09	1.88	0.03
YSF4	SOI 9	#12	56.19		0.21	0.35	13.24	1.11	0.07	1.44	27.40	0.94	0.08	0.02	<	0.10	1.95	0.02
YSF4	SOI 2	#3	54.85	<	0.35	0.51	13.42	1.08	0.08	1.47	28.23	0.98	0.08	0.03	0.01	0.11	2.06	0.04

Sample	Area	Point	EDS in atomic%									formula (4 oxygens)						
			O	Na	Mg	Al	Si	P	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al
YSF29	SOI3	#8	56.88		<	0.26	12.84	1.16		1.16	27.69	0.90	0.08	<	<	0.08	1.95	0.02
YSF8	SOI6	#14	53.40	<	0.75	0.38	14.58	1.09		3.24	26.56	1.09	0.08	0.06	<	0.24	1.99	0.03
YSF10	SOI3	#8	56.75	0.27	0.38	0.39	12.68	1.17	0.07	1.49	26.81	0.89	0.08	0.03	<	0.10	1.89	0.03
YSF29	SOI3	#10	56.62		0.60	0.37	12.93	1.17		1.22	27.08	0.91	0.08	0.04	<	0.09	1.91	0.03
YSF5	SOI 5	#7	57.05		0.40	0.45	12.70	1.21	0.09	0.80	27.30	0.89	0.08	0.03	0.01	0.06	1.91	0.03
YSF25	SOI1	#5	57.40		0.62	0.34	12.77	1.22	0.09	1.51	26.04	0.89	0.09	0.04	0.01	0.11	1.81	0.02
YSF2	SOI10	#19	60.34	<	0.20	0.41	12.69	1.29		1.24	23.83	0.84	0.09	0.01	<	0.08	1.58	0.03
YSF2	SOI7	#11	56.76	<	0.21	0.39	12.89	1.22		1.42	27.11	0.91	0.09	0.01	<	0.10	1.91	0.03
YSF4	SOI 2	#2	55.05	<	0.55	0.43	13.40	1.19	0.07	1.60	27.71	0.97	0.09	0.04	<	0.12	2.01	0.03
YSF25	SOI2	#15	56.37		0.49	0.47	12.98	1.22	0.09	1.53	26.85	0.92	0.09	0.04	0.01	0.11	1.91	0.03
YSF27	SOI11	#14	57.67	<	0.25	0.29	12.76	1.26	<	1.48	26.29	0.88	0.09	0.02	<	0.10	1.82	0.02
YSF29	SOI3	#24	57.49		<	0.39	12.53	1.30		1.06	27.22	0.87	0.09	<	<	0.07	1.89	0.03
YSF2	SOI9	#8	57.16	<	0.40	0.43	12.52	1.31		1.53	26.64	0.88	0.09	0.03	<	0.11	1.86	0.03
YSF25	SOI1	#4	57.16		0.51	0.42	12.69	1.32		1.59	26.31	0.89	0.09	0.04	<	0.11	1.84	0.03
YSF3	SOI10	#5	54.79		0.35	0.51	13.55	1.30		1.48	28.03	0.99	0.09	0.03	<	0.11	2.05	0.04
YSF2	SOI9	#5	56.61		0.41	0.40	12.58	1.34	0.07	1.60	27.00	0.89	0.10	0.03	0.01	0.11	1.91	0.03
YSF3	SOI10	#2	54.92		<	0.36	13.63	1.34		1.45	28.31	0.99	0.10	<	<	0.11	2.06	0.03
YSF5	SOI 2	#2	58.35		0.17	0.33	12.68	1.52	0.09	0.73	26.13	0.87	0.10	0.01	0.01	0.05	1.79	0.02
YSF2	SOI9	#6	57.25	0.23	0.48	0.52	12.27	1.50	<	1.48	26.28	0.86	0.10	0.03	<	0.10	1.84	0.04
YSF27	SOI13	#1	58.16		0.37	0.32	12.56	1.52	0.09	1.46	25.53	0.86	0.10	0.03	0.01	0.10	1.76	0.02
YSF2	SOI7	#10	60.04		0.14	0.41	12.58	1.58	0.08	1.31	23.86	0.84	0.11	0.01	0.01	0.09	1.59	0.03
YSF29	SOI6	#11	58.02		0.27	0.50	12.22	1.53		1.04	26.41	0.84	0.11	0.02	<	0.07	1.82	0.03
YSF5	SOI 2	#1	60.72		0.32	0.44	12.88	1.61		0.78	23.24	0.85	0.11	0.02	<	0.05	1.53	0.03
YSF29	SOI10	#19	57.20		0.17	0.28	12.69	1.52		1.04	27.11	0.89	0.11	0.01	<	0.07	1.90	0.02
YSF5	SOI 5	#8	57.20		0.47	0.44	12.64	1.52	<	0.77	26.96	0.88	0.11	0.03	<	0.05	1.89	0.03
YSF10	SOI3	#9	57.48		0.17	0.28	12.43	1.54	0.09	1.33	26.69	0.87	0.11	0.01	0.01	0.09	1.86	0.02
YSF29	SOI3	#9	56.70		0.47	0.36	12.68	1.52		1.14	27.13	0.89	0.11	0.03	<	0.08	1.91	0.03
YSF27	SOI11	#12	58.21		<	0.30	12.39	1.60	0.08	1.36	26.05	0.85	0.11	<	0.01	0.09	1.79	0.02
YSF27	SOI16	#1	57.47		0.30	0.45	12.52	1.62		1.55	26.10	0.87	0.11	0.02	<	0.11	1.82	0.03
YSF9	SOI3	#1	57.23		0.18	0.37	11.51	1.69		1.15	27.87	0.80	0.12	0.01	<	0.08	1.95	0.03
YSF2	SOI10	#20	59.72	<	0.24	0.33	12.26	1.76		1.27	24.35	0.82	0.12	0.02	<	0.09	1.63	0.02
YSF3	SOI10	#6	54.49		0.32	0.43	13.33	1.62		1.48	28.33	0.98	0.12	0.02	<	0.11	2.08	0.03
YSF29	SOI10	#21	57.21		0.22	0.25	12.38	1.83		1.09	27.02	0.87	0.13	0.02	<	0.08	1.89	0.02
YSF2	SOI7	#9	57.04		0.24	0.35	12.19	1.96		1.30	26.92	0.85	0.14	0.02	<	0.09	1.89	0.02
YSF9	SOI2	#7	57.90	0.24	0.38	0.37	11.80	2.07	0.11	1.41	25.70	0.81	0.14	0.03	0.01	0.10	1.78	0.03
YSF29	SOI6	#12	58.12		0.24	0.44	11.77	2.08		1.16	26.19	0.81	0.14	0.02	<	0.08	1.80	0.03
YSF9	SOI2	#6	57.88	<	0.21	0.41	11.86	2.19	0.11	1.34	26.01	0.82	0.15	0.01	0.01	0.09	1.80	0.03

Sample	Area	Point	EDS in atomic%									formula (4 oxygens)						
			O	Na	Mg	Al	Si	P	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al
YSF9	SOI6	#6	56.64		0.27	0.46	12.21	2.24	0.10	1.41	26.68	0.86	0.16	0.02	0.01	0.10	1.88	0.03
YSF4	SOI 2	#4	55.48		<	0.30	12.54	2.24	<	1.20	28.25	0.90	0.16	<	<	0.09	2.04	0.02
YSF4	SOI 2	#6	55.69	0.25	0.18	0.36	12.27	2.42	0.08	1.31	27.45	0.88	0.17	0.01	0.01	0.09	1.97	0.03
YSF3	SOI10	#4	55.53		<	0.34	12.65	2.58		1.37	27.53	0.91	0.19	<	<	0.10	1.98	0.02
YSF29	SOI3	#23	57.55		<	0.34	11.29	2.75		1.06	27.02	0.78	0.19	<	<	0.07	1.88	0.02
YSF29	SOI10	#20	57.09		0.18	0.22	11.65	2.77		1.11	26.98	0.82	0.19	0.01	<	0.08	1.89	0.02
YSF29	SOI6	#13	58.22			0.31	11.18	2.85	0.13	1.08	26.24	0.77	0.20	<	0.01	0.07	1.80	0.02
YSF3	SOI11	#19	55.01		0.21	0.43	12.30	2.79		1.36	27.89	0.89	0.20	0.02	<	0.10	2.03	0.03
YSF27	SOI11	#15	58.69	<	<	0.37	10.38	3.51	0.09	1.26	25.71	0.71	0.24	<	0.01	0.09	1.75	0.03
YSF4	SOI 4	#20	55.96	<	<	0.33	11.21	3.64	0.07	1.34	27.45	0.80	0.26	<	<	0.10	1.96	0.02
YSF2	SOI7	#8	57.84	<	<	0.33	10.45	3.80	<	1.34	26.25	0.72	0.26	<	<	0.09	1.82	0.02
YSF4	SOI 4	#19	56.28	<	<	0.25	10.98	3.80	0.06	1.35	27.27	0.78	0.27	<	<	0.10	1.94	0.02
YSF3	SOI11	#16	55.61		<	0.33	11.36	3.79	0.10	1.24	27.57	0.82	0.27	<	0.01	0.09	1.98	0.02
YSF3	SOI11	#17	55.53		0.21	0.34	11.47	3.82	0.07	1.20	27.37	0.83	0.27	0.01	0.01	0.09	1.97	0.02
YSF3	SOI11	#18	55.87		<	0.39	11.20	3.98		1.30	27.24	0.80	0.29	<	<	0.09	1.95	0.03
YSF10	SOI10	#11	57.41			0.35	10.17	4.29	0.12	1.31	26.36	0.71	0.30	<	0.01	0.09	1.84	0.02
YSF4	SOI 4	#18	55.86	0.27	<	0.26	10.68	4.32	0.08	1.33	27.20	0.76	0.31	<	0.01	0.10	1.95	0.02
YSF27	SOI11	#8	58.64			0.32	9.34	4.96	0.11	1.29	25.34	0.64	0.34	<	0.01	0.09	1.73	0.02
YSF25	SOI2	#12	58.31		<	0.29	9.40	5.42	0.08	1.17	25.34	0.64	0.37	<	0.01	0.08	1.74	0.02
YSF27	SOI10	#7	59.46	<		0.32	8.76	5.58	0.08	1.33	24.48	0.59	0.38	<	0.01	0.09	1.65	0.02
YSF27	SOI11	#11	59.24	<	<	0.25	8.16	6.42	0.10	1.36	24.48	0.55	0.43	<	0.01	0.09	1.65	0.02
YSF27	SOI11	#10	59.29		<	0.27	8.03	6.45	0.10	1.29	24.57	0.54	0.44	<	0.01	0.09	1.66	0.02
YSF27	SOI10	#19	59.42			0.27	7.53	6.98	0.10	1.37	24.33	0.51	0.47	<	0.01	0.09	1.64	0.02
YSF27	SOI10	#32	59.87	<	<	0.23	7.27	7.13	0.10	1.25	24.14	0.49	0.48	<	0.01	0.08	1.61	0.02
YSF27	SOI10	#6	59.68			0.30	7.30	7.25	0.12	1.27	24.08	0.49	0.49	<	0.01	0.09	1.61	0.02
YSF27	SOI10	#31	60.06	<	<	0.25	7.15	7.32	0.14	1.31	23.78	0.48	0.49	<	0.01	0.09	1.58	0.02
YSF27	SOI10	#9	60.66			<	6.38	8.18	0.16	1.25	23.37	0.42	0.54	<	0.01	0.08	1.54	<
YSF27	SOI10	#15	60.10	0.26		0.23	6.33	8.13	0.16	1.27	23.52	0.42	0.54	<	0.01	0.08	1.57	0.02
YSF27	SOI10	#18	59.90			0.25	6.26	8.24	0.21	1.13	24.01	0.42	0.55	<	0.01	0.08	1.60	0.02
YSF25	SOI4	#9	59.12	0.28	0.16	0.15	6.37	8.22	0.16	1.44	24.10	0.43	0.56	0.01	0.01	0.10	1.63	0.01
YSF27	SOI10	#23	60.74			0.12	5.49	9.04	0.21	1.28	23.12	0.36	0.60	<	0.01	0.08	1.52	0.01
YSF27	SOI10	#8	60.53	0.26		0.22	4.90	9.73	0.19	1.15	23.03	0.32	0.64	<	0.01	0.08	1.52	0.01
YSF27	SOI10	#13	60.46	0.36		0.20	4.75	9.83	0.24	1.06	23.11	0.31	0.65	<	0.02	0.07	1.53	0.01
YSF27	SOI10	#20	60.42	0.32	<	0.20	4.34	10.31	0.24	1.09	23.06	0.29	0.68	<	0.02	0.07	1.53	0.01
YSF27	SOI10	#21	60.50			0.38	3.91	10.63	0.27	1.08	23.22	0.26	0.70	<	0.02	0.07	1.54	0.03
YSF29	SOI3	#21	59.69	0.25	<	0.21	3.82	10.85	0.11	1.33	23.75	0.26	0.73	<	0.01	0.09	1.59	0.01
YSF27	SOI10	#12	60.20	<		0.27	3.71	11.19	0.33	1.11	23.18	0.25	0.74	<	0.02	0.07	1.54	0.02

Sample	Area	Point	EDS in atomic%									formula (4 oxygens)						
			O	Na	Mg	Al	Si	P	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al
YSF29	SOI6	#4	61.20	0.22		0.13	3.16	11.38	0.60	1.15	22.16	0.21	0.74	<	0.04	0.08	1.45	0.01
YSF29	SOI6	#2	60.51	<	<	0.11	3.16	11.82	0.15	1.14	23.10	0.21	0.78	<	0.01	0.08	1.53	0.01
YSF3	SOI11	#10	59.11			0.18	3.14	12.26	1.26	1.32	22.73	0.21	0.83	<	0.09	0.09	1.54	0.01
YSF3	SOI11	#8	57.81	<		0.31	3.37	12.68	0.39	1.20	24.24	0.23	0.88	<	0.03	0.08	1.68	0.02
YSF3	SOI11	#6	58.03	<		0.21	3.09	13.09	0.36	1.24	23.97	0.21	0.90	<	0.03	0.09	1.65	0.01

Table 10: EDS Micro-analyses of the constituent minerals of refining slags (2): alkali-bearing phosphate.

Sample	Area	Point	EDS in atomic%										formula (8 oxygens)							
			O	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al	Na+K
YSF27	SOI13	#6	62.42	2.20	0.28	0.35	0.25	15.02	1.42	4.17	2.13	11.77	0.03	1.93	0.04	0.53	0.27	1.51	0.04	0.46
YSF27	SOI16	#3	61.75	1.96	0.27	0.45	0.36	15.09	1.58	3.85	2.59	12.11	0.05	1.96	0.03	0.50	0.34	1.57	0.06	0.46
YSF29	SOI6	#8	61.59	0.99	<		0.40	14.24	1.69	3.92	1.48	15.68	0.05	1.85	<	0.51	0.19	2.04	<	0.35
YSF4	SOI 3	#15	57.54	1.59		<	0.96	14.56	2.39	2.67	1.55	18.76	0.13	2.02	<	0.37	0.22	2.61	<	0.55
YSF29	SOI6	#7	60.47	1.32	0.12	0.10	0.65	14.01	2.57	2.73	1.41	16.61	0.09	1.85	0.02	0.36	0.19	2.20	0.01	0.52
YSF2	SOI8	#4	59.37	1.71	<	0.15	0.94	14.22	2.77	2.56	1.59	16.68	0.13	1.92	<	0.35	0.21	2.25	0.02	0.60
YSF4	SOI 3	#10	57.22	1.45		0.11	0.98	14.73	2.82	2.57	1.61	18.52	0.14	2.06	<	0.36	0.23	2.59	0.02	0.60
YSF10	SOI4	#6	60.07	1.47	0.18	<	0.69	14.17	2.83	2.94	1.76	15.90	0.09	1.89	0.02	0.39	0.23	2.12	<	0.57
YSF27	SOI10	#10	60.65	1.43	<	<	0.88	13.78	2.83	3.28	1.50	15.65	0.12	1.82	<	0.43	0.20	2.06	<	0.56
YSF3	SOI11	#12	58.15	1.28	0.14	<	0.85	14.90	2.84	3.04	1.70	17.10	0.12	2.05	0.02	0.42	0.23	2.35	<	0.57
YSF2	SOI8	#5	58.52	1.37	<	<	1.03	13.50	2.86	2.23	1.55	18.92	0.14	1.85	<	0.31	0.21	2.59	<	0.58
YSF27	SOI10	#11	60.61	1.30		0.11	1.13	13.60	2.89	3.54	1.37	15.44	0.15	1.80	<	0.47	0.18	2.04	0.02	0.55
YSF2	SOI10	#8	59.34	1.49	0.25	<	0.84	14.18	2.92	2.40	1.89	16.69	0.11	1.91	0.03	0.32	0.26	2.25	<	0.59
YSF27	SOI10	#16	60.62	1.22		0.11	1.06	13.59	2.99	3.39	1.44	15.59	0.14	1.79	<	0.45	0.19	2.06	0.01	0.56
YSF10	SOI3	#3	58.68	1.44	0.16	0.30	0.76	13.64	3.01	2.83	1.70	17.48	0.10	1.86	0.02	0.39	0.23	2.38	0.04	0.61
YSF29	SOI6	#14	59.67	1.25	<	<	0.86	14.28	3.02	2.53	1.54	16.85	0.12	1.91	<	0.34	0.21	2.26	<	0.57
YSF2	SOI8	#8	59.04	1.28	0.13	0.13	1.02	13.91	3.06	2.43	1.67	17.32	0.14	1.88	0.02	0.33	0.23	2.35	0.02	0.59
YSF2	SOI10	#25	59.54	1.20	0.17	<	0.88	14.13	3.09	2.37	1.81	16.80	0.12	1.90	0.02	0.32	0.24	2.26	<	0.58
YSF29	SOI3	#3	59.48	1.27	<	<	0.77	14.47	3.11	2.57	1.66	16.67	0.10	1.95	<	0.35	0.22	2.24	<	0.59
YSF3	SOI11	#11	57.86	1.61	0.16	<	0.96	14.76	3.14	2.72	1.62	17.16	0.13	2.04	0.02	0.38	0.22	2.37	<	0.66
YSF4	SOI 4	#11	57.98	1.72	<	<	0.88	14.54	3.17	2.45	1.61	17.65	0.12	2.01	<	0.34	0.22	2.43	<	0.67
YSF4	SOI 5	#6	57.68	1.59	0.15	0.10	0.65	15.01	3.18	2.51	1.73	17.39	0.09	2.08	0.02	0.35	0.24	2.41	0.01	0.66
YSF2	SOI8	#7	59.45	1.25	<	<	0.97	13.95	3.18	2.64	1.74	16.71	0.13	1.88	<	0.36	0.23	2.25	<	0.60
YSF2	SOI8	#16	59.45	1.43	0.14	<	0.90	13.97	3.18	2.59	1.73	16.60	0.12	1.88	0.02	0.35	0.23	2.23	<	0.62
YSF29	SOI10	#15	59.85	1.52	<	<	0.77	14.20	3.18	2.70	1.45	16.34	0.10	1.90	<	0.36	0.19	2.18	<	0.63
YSF2	SOI8	#6	59.43	1.31	0.13	<	1.06	14.04	3.19	2.62	1.73	16.50	0.14	1.89	0.02	0.35	0.23	2.22	<	0.60
YSF2	SOI10	#7	59.85	1.04	0.21		0.89	14.03	3.19	2.46	1.94	16.32	0.12	1.88	0.03	0.33	0.26	2.18	<	0.57
YSF10	SOI3	#2	59.58	1.18	0.23	<	0.75	14.29	3.23	2.90	1.88	15.97	0.10	1.92	0.03	0.39	0.25	2.14	<	0.59
YSF2	SOI7	#18	58.98	1.25	<	<	0.83	14.51	3.24	2.65	1.80	16.74	0.11	1.97	<	0.36	0.24	2.27	<	0.61
YSF10	SOI4	#9	59.51	1.18	0.17	<	0.74	14.26	3.25	3.06	1.88	15.97	0.10	1.92	0.02	0.41	0.25	2.15	<	0.59
YSF29	SOI10	#1	59.70	1.43	<	<	0.67	14.18	3.26	2.86	1.47	16.44	0.09	1.90	<	0.38	0.20	2.20	<	0.63
YSF4	SOI 4	#22	57.62	1.49	0.15	0.18	0.95	14.75	3.29	2.58	1.65	17.35	0.13	2.05	0.02	0.36	0.23	2.41	0.02	0.66
YSF4	SOI 9	#5	58.42	1.21	0.15		0.90	14.56	3.31	2.81	1.90	16.72	0.12	1.99	0.02	0.38	0.26	2.29	<	0.62
YSF10	SOI10	#7	59.04	1.19			0.96	14.15	3.33	3.44	1.66	16.23	0.13	1.92	<	0.47	0.22	2.20	<	0.61

Sample	Area	Point	EDS in atomic%											formula (8 oxygens)						
			O	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al	Na+K
YSF10	SOI10	#8	59.47	1.11			0.88	14.07	3.36	3.46	1.57	16.09	0.12	1.89	<	0.47	0.21	2.16	<	0.60
YSF10	SOI10	#6	59.69	1.01		<	0.84	14.07	3.43	3.65	1.65	15.67	0.11	1.89	<	0.49	0.22	2.10	<	0.59
YSF4	SOI 9	#6	58.08	1.12		<	0.94	14.48	3.48	2.79	1.84	17.27	0.13	1.99	<	0.38	0.25	2.38	<	0.63

Table 11: EDS Micro-analyses of the constituent minerals of refining slags (3): iron-calcium-manganese phosphates.

Sample	Area	Point	EDS in atomic%										formula (8 oxygens)							
			O	Na	Mg	Al	Si	P	K	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al	Na+K
YSF27	SOI10	#27	64.69	0.84	<	0.32	0.50	12.61	0.17	16.14	0.31	4.42	0.06	1.56	<	2.00	0.04	0.55	0.04	0.12
YSF27	SOI10	#28	62.72	1.13		0.13	0.13	14.02	0.16	18.10	0.21	3.39	0.02	1.79	<	2.31	0.03	0.43	0.02	0.16
YSF27	SOI10	#29	62.60	0.29	<	0.31		14.58	0.19	8.21	1.05	12.78	<	1.86	<	1.05	0.13	1.63	0.04	0.06
YSF29	SOI6	#3	61.88			0.12		14.53	0.05	7.67	1.41	14.33	<	1.88	<	0.99	0.18	1.85	0.02	0.01
YSF9	SOI2	#9	61.56	<	0.18	<	0.14	15.11		7.30	1.87	13.85	0.02	1.96	0.02	0.95	0.24	1.80	<	<
YSF25	SOI4	#10	61.46		0.13	<	0.19	14.94		7.13	1.60	14.55	0.02	1.94	0.02	0.93	0.21	1.89	<	<
YSF29	SOI6	#1	61.89		<		0.16	14.95	0.08	7.13	1.52	14.27	0.02	1.93	<	0.92	0.20	1.84	<	0.01
YSF9	SOI2	#1	62.39	<	0.21	<	0.17	14.84		7.18	1.80	13.40	0.02	1.90	0.03	0.92	0.23	1.72	<	<
YSF3	SOI11	#7	59.76			0.12	0.46	15.27		6.62	1.54	16.22	0.06	2.04	<	0.89	0.21	2.17	0.02	<
YSF25	SOI2	#11	60.48		<	<	0.27	15.26	0.08	6.62	1.61	15.67	0.04	2.02	<	0.88	0.21	2.07	<	0.01
YSF3	SOI11	#5	58.38			<	0.59	15.98		6.21	1.60	17.23	0.08	2.19	<	0.85	0.22	2.36	<	<
YSF25	SOI2	#3	61.24			<	0.21	15.07	0.10	6.37	1.51	15.51	0.03	1.97	<	0.83	0.20	2.03	<	0.01
YSF25	SOI4	#11	62.64			0.09	0.09	14.76	0.06	6.49	1.59	14.29	0.01	1.88	<	0.83	0.20	1.83	0.01	0.01
YSF2	SOI9	#21	61.22	0.48	0.33	<	0.28	14.62	0.39	6.13	2.29	14.25	0.04	1.91	0.04	0.80	0.30	1.86	<	0.11
YSF29	SOI6	#15	63.37				0.53	14.30	0.12	6.09	1.37	14.21	0.07	1.81	<	0.77	0.17	1.79	<	0.02
YSF2	SOI8	#9	61.64	0.23		0.13	0.52	14.37		5.91	1.47	15.73	0.07	1.87	<	0.77	0.19	2.04	0.02	0.03
YSF2	SOI8	#10	59.58	0.34		0.16	0.81	14.65		5.65	1.59	17.22	0.11	1.97	<	0.76	0.21	2.31	0.02	0.05
YSF27	SOI13	#5	62.45	<	0.19	<		14.98		5.70	3.46	13.23	<	1.92	0.02	0.73	0.44	1.69	<	<
YSF27	SOI13	#5	62.45	<	0.19	<		14.98		5.70	3.46	13.23	<	1.92	0.02	0.73	0.44	1.69	<	<
YSF9	SOI6	#7	61.04		0.18	<	0.46	15.28		5.30	1.90	15.86	0.06	2.00	0.02	0.69	0.25	2.08	<	<
YSF10	SOI4	#1	60.51			0.10	1.65	13.43		5.19	1.56	17.56	0.22	1.78	<	0.69	0.21	2.32	0.01	<
YSF9	SOI6	#2	60.40		<	<	0.73	15.01		4.69	1.86	17.31	0.10	1.99	<	0.62	0.25	2.29	<	<
YSF8	SOI8	#20	57.96	<	0.91		0.88	15.96		1.28	6.13	16.87	0.12	2.20	0.12	0.18	0.85	2.33	<	<
YSF8	SOI8	#10	57.08		0.95	<	0.55	16.53		1.40	6.52	16.97	0.08	2.32	0.13	0.20	0.91	2.38	<	<
YSF8	SOI8	#24	56.95		0.92	0.13	0.53	16.50		1.40	6.74	16.82	0.08	2.32	0.13	0.20	0.95	2.36	0.02	<
YSF8	SOI8	#21	57.00	<	1.09	<	0.82	16.52		1.38	6.64	16.55	0.11	2.32	0.15	0.19	0.93	2.32	<	<
YSF8	SOI6	#12	57.04		0.84	<	0.48	16.66		2.15	7.35	15.47	0.07	2.34	0.12	0.30	1.03	2.17	<	<

Table 12: EDS Micro-analyses of the constituent minerals of refining slags (4): phosphoran iscorite.

Sample	Area	Point	EDS in atomic%								formula (10 oxygens)							
			O	Al	Si	P	Ti	V	Mn	Fe	Si	P	Mn	Fe ²⁺	Al	Fe ³⁺	Ti	V
YSF2	SOI10	#21	53.73	0.64	2.04	2.48	0.58	0.29	0.57	39.66	0.38	0.46	0.11	4.89	0.12	2.49	0.11	0.05
YSF30	SOI11	#4	52.85	0.75	1.77	2.63	0.23	0.11	0.49	41.16	0.34	0.50	0.09	4.91	0.14	2.88	0.04	0.02
YSF29	SOI6	#9	53.78	0.65	1.88	2.83	0.45	<	0.34	40.07	0.35	0.53	0.06	4.94	0.12	2.51	0.08	<
YSF4	SOI 2	#8	51.73	1.05	2.54	2.74	0.78	<	0.48	40.68	0.49	0.53	0.09	4.91	0.20	2.96	0.15	<
YSF29	SOI3	#1	53.39	0.52	1.60	2.90	0.35	0.25	0.45	40.55	0.30	0.54	0.08	4.92	0.10	2.68	0.06	0.05
YSF29	SOI10	#9	53.38	0.53	1.77	2.91	0.17	0.21	0.40	40.64	0.33	0.54	0.07	4.93	0.10	2.69	0.03	0.04
YSF25	SOI4	#15	53.71	0.56	1.75	2.93	0.27	0.16	0.51	40.10	0.33	0.54	0.10	4.90	0.11	2.56	0.05	0.03
YSF2	SOI10	#4	53.23	0.55	1.81	2.91	0.50	0.34	0.54	40.13	0.34	0.55	0.10	4.90	0.10	2.64	0.09	0.06
YSF10	SOI10	#5	54.09	0.67	2.24	3.06	0.70	<	0.48	38.76	0.41	0.57	0.09	4.91	0.12	2.25	0.13	<
YSF3	SOI11	#2	51.51	0.68	1.81	3.05	0.40	<	0.60	41.94	0.35	0.59	0.12	4.88	0.13	3.26	0.08	<
YSF4	SOI 5	#11	51.51	0.61	1.80	3.09	0.72	<	0.72	41.55	0.35	0.60	0.14	4.86	0.12	3.20	0.14	<
YSF4	SOI 5	#1	51.88	0.75	1.61	3.18	0.53	0.11	0.52	41.41	0.31	0.61	0.10	4.90	0.14	3.08	0.1	0.02
YSF4	SOI 4	#5	51.44	0.76	1.87	3.18	0.41	<	0.59	41.74	0.36	0.62	0.11	4.89	0.15	3.23	0.08	<
YSF2	SOI9	#17	53.16	0.42	1.20	3.47	0.42	0.34	0.68	40.31	0.23	0.65	0.13	4.87	0.08	2.71	0.08	0.06
YSF4	SOI 9	#17	51.13	0.49	1.26	3.42	0.39	0.30	0.54	42.47	0.25	0.67	0.11	4.89	0.10	3.41	0.08	0.06

Table 13: Major element chemical composition of refining microresidues (sample YSF11)

Particle			Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO	
YSF11			XRF	0.04	0.26	2.81	13.01	2.95	0.08		0.22	0.57	0.34	0.35	0.13	1.35	77.89
SOI2	#3	S1	EDS	0.29	<	2.52	17.47	5.53		0.21	0.63	0.35	0.36		2.61	66.08	
SOI4	#1	S2	EDS	<	<	3.13	18.64	5.27	0.53	0.15	0.58	0.45	0.55	0.28	1.30	68.02	
SOI7	#1	S3	EDS	0.32	0.22	2.63	24.90	2.03		0.28	0.88	0.35	0.32		1.38	64.81	
SOI8	#2	S4	EDS	<	0.28	2.41	18.27	4.42		0.19	0.62	0.28	0.21		2.25	68.70	
SOI9	#1	S5	EDS	<	0.35	2.79	15.19	5.64		0.15	0.98	0.56	0.56	0.36	2.49	67.77	
SOI10	#1	S6	EDS	0.32	0.80	6.40	21.13	5.25		0.17	1.97	0.50	0.53		1.65	58.77	
SOI11	#2	S7	EDS	<	0.25	2.40	14.33	6.69	0.14	0.16	0.74	0.26	0.35		2.21	69.97	
SOI27	#1	S8	EDS	<	0.30	4.26	22.10	3.49		0.32	0.78	0.54	0.30		1.19	65.31	
SOI30	#1	S9	EDS		0.21	3.07	11.79	6.21		0.19	0.40	0.45	0.30	0.40	1.90	72.18	
SOI30	#2	S9	EDS	<	<	2.79	15.64	8.65		0.23	0.58	0.21	<	0.19	2.29	66.81	
SOI32	#5	S10	EDS	0.25	0.25	2.67	21.01	5.56		0.19	0.55	0.32	<	0.16	0.70	66.11	
SOI34	#2	S11	EDS	0.28	0.40	3.58	15.93	8.68	0.13	0.27	1.03	<	<		3.65	65.05	
SOI36	#3	S12	EDS	0.42	0.31	3.65	16.51	6.62		0.38	0.63	0.41	0.33		2.12	65.49	
SOI38	#1	S13	EDS	<	<	2.02	16.12	5.18	0.09	0.17	0.40	0.36	0.20	0.21	2.03	70.28	
SOI40	#1	S14	EDS	<	0.28	3.55	15.75	5.85		0.34	0.66	0.32	0.29	0.15	2.11	68.51	
SOI42	#1	S15	EDS	0.26	0.56	4.56	18.74	7.65	<	0.32	0.96	0.46	1.12	0.27	3.03	61.31	
SOI44	#1	S16	EDS	0.35	0.40	2.46	21.46	2.49	0.16	0.17	1.47	0.37	0.20	<	1.47	68.52	
SOI46	#1	S17	EDS	0.24	0.39	4.89	25.44	4.79	0.21	0.41	0.90	0.35	0.60	0.29	1.05	59.67	
SOI48	#1	S18	EDS	<	0.37	4.89	16.76	4.98	0.48	0.34	0.94	0.29	0.33	0.16	2.10	66.38	
SOI50	#1	S19	EDS	<	0.40	4.15	19.16	4.73	0.16	0.26	1.09	0.47	0.36	0.27	2.33	65.38	
SOI52	#1	S20	EDS	<	0.28	2.70	19.21	7.68		0.20	0.82	0.32	0.35		3.00	64.29	
SOI54	#1	S21	EDS		0.34	2.96	16.41	8.31		0.18	0.64	0.31	0.42	0.30	2.93	65.94	
SOI56	#1	S22	EDS		0.25	4.40	24.66	2.47		0.35	0.71	0.39	<		1.14	63.82	
SOI58	#1	S23	EDS	<	0.45	3.90	17.68	4.09		0.16	1.13	0.32	0.53	0.18	2.43	68.88	
		<i>average</i>	<i>EDS</i>		<i>0.35</i>	<i>3.45</i>	<i>18.51</i>	<i>5.51</i>		<i>0.28</i>	<i>0.81</i>	<i>0.37</i>	<i>0.41</i>	<i>0.25</i>	<i>2.06</i>	<i>66.17</i>	

Table 14: Major element chemical composition of refining microresidues (sample YSF11a)

Particle				Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO
YSF11a																	
SOI4	#1	S44	EDS			2.53	5.33	0.78			0.21	0.51	0.21	0.34	<	<	88.91
SOI4	#2	S45	EDS			0.30	0.25	2.46									90.55
SOI5	#1	S46	EDS	<		1.93	11.51	2.62		0.13	0.21	0.21	0.19	0.24	<	1.24	75.58
SOI5	#2	S47	EDS				0.49										89.39
SOI5	#3	S48	EDS			<	0.23										88.11
SOI5	#4	S49	EDS			0.22	<	0.23									86.54
SOI5	#5	S50	EDS			0.33	<	0.70									90.38
SOI5	#6	S51	EDS			0.65	0.54	0.26	<								82.71
SOI5	#7	S52	EDS			<	<										89.59
SOI5	#8	S53	EDS			0.32	<										89.34
SOI6	#1	S54	EDS			0.35	1.10	0.47	<								90.55
SOI6	#2	S55	EDS			<	<		0.47								88.48
SOI6	#3	S56	EDS			0.44	0.90	<	<								90.52
SOI6	#4	S57	EDS			<											93.51
SOI6	#5	S58	EDS					1.17	0.14								90.39
SOI6	#6	S59	EDS			0.26		<	<								87.63
SOI6	#7	S60	EDS			0.45	0.44	0.41	<								85.78
SOI6	#8	S61	EDS			0.36	<	0.75	0.09								84.14
SOI6	#9	S62	EDS			0.50	<	0.22	0.32								82.75
SOI6	#10	S63	EDS			2.04											86.79
SOI6	#11	S64	EDS			0.25	0.25										84.28
SOI6	#12	S65	EDS		<	0.37	<		0.19								86.00
SOI6	#13	S66	EDS			0.29	<	0.83	0.12	<							84.65
SOI6	#14	S67	EDS	<	<	0.47		0.31	0.60								80.60
SOI7	#1	S68	EDS			<	0.52	0.22			0.13						91.16
SOI7	#2	S69	EDS			0.27	0.53	0.30									89.94
SOI7	#3	S70	EDS						0.12								88.38
SOI7	#4	S71	EDS														90.63
SOI8	#1	S72	EDS			0.23											89.54
SOI8	#2	S73	EDS			<		0.28									91.24
SOI8	#3	S74	EDS			<	<	<			<						88.86
SOI8	#4	S75	EDS			0.31	0.23	0.43									89.23
SOI8	#5	S76	EDS			<	0.21	0.44									87.39
SOI8	#6	S77	EDS			0.23	0.26										87.23
SOI8	#7	S78	EDS			0.31	<	0.38	0.20		0.19						91.76
SOI8	#8	S79	EDS			0.21	<	<			0.17						86.21

SOI8	#9	S80	EDS	0.22	0.29	0.47	0.18	86.88
SOI8	#10	S81	EDS	<	<	0.53	0.26	88.73
		<i>average</i>	<i>EDS</i>	<i>0.55</i>	<i>1.44</i>	<i>0.68</i>		<i>87.75</i>

Table 15: Major element chemical composition of refining microresidues (sample YSF12)

Particle			Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO	
YSF12			XRF	0.08	0.32	3.30	17.07	3.09	0.32		0.31	0.96	0.39	0.33	0.10	1.22	72.51
SOI3	#1	S24	EDS	0.26	0.33	2.92	18.88	2.86	0.11		0.28	0.88	0.40	0.30		1.15	66.14
SOI5	#1	S25	EDS	<	<	1.95	20.01	5.49		0.11	0.52	0.32	0.42	0.27	0.84	65.62	
SOI6	#1	S26	EDS	<	<	3.47	18.46	4.58		0.33	0.51	0.30	<		1.03	66.42	
SOI8	#1	S27	EDS	<	0.47	2.13	22.31	5.21		0.18	0.65	0.34	0.30		1.31	62.37	
SOI10	#1	S28	EDS	0.33	0.31	4.64	18.23	4.72	0.10	0.39	0.79	0.57	0.62	0.25	2.07	62.94	
SOI11	#1	S29	EDS	<	0.24	2.72	18.91	3.48		0.22	0.61	0.22	<		1.14	67.21	
SOI12	#1	S30	EDS	<	<	0.87	11.46	1.71		<	0.25	<	0.22	0.20	0.43	78.52	
SOI14	#1	S31	EDS	<	0.30	3.10	22.52	4.61		0.29	0.61	0.40	0.32	0.19	0.86	62.22	
SOI14	#2	S32	EDS	<	0.30	2.92	21.40	3.05		0.23	0.82	0.30	<	0.15	0.76	64.92	
SOI16	#1	S33	EDS	<	0.30	2.28	21.24	4.81		0.16	0.60	0.29	0.47	0.17	2.49	62.17	
SOI17	#1	S34	EDS	<	0.40	4.57	22.65	2.94		0.33	0.76	0.35	0.20		1.00	61.34	
SOI18	#1	S35	EDS	<	<	2.33	15.52	3.44		0.14	0.25	0.20	0.26	0.17	1.42	70.51	
SOI18	#2	S36	EDS	0.34	0.27	2.75	16.24	2.52		0.23	0.46	0.21	0.21	<	0.96	70.91	
SOI19	#8	S37	EDS	0.30	0.36	3.17	21.33	3.71	0.11	0.29	0.99	0.24	0.32	0.16	0.94	63.19	
SOI22	#3	S38	EDS	<	0.28	3.12	15.66	4.02	0.14	0.22	0.71	0.28	0.21		0.90	69.73	
SOI24	#1	S39	EDS		<	3.23	16.54	4.26		0.25	0.35	0.47	0.73	0.29	1.73	68.06	
SOI24	#2	S40	EDS	0.30	0.25	3.44	20.50	2.15		0.27	0.93	0.35	0.29		1.45	64.97	
SOI25	#1	S41	EDS	0.31	0.49	4.33	19.93	3.66		0.32	1.05	0.43	0.61	0.27	1.95	62.40	
SOI25	#3	S42	EDS	<	0.47	5.22	16.08	7.03		0.37	0.67	0.47	0.77	0.38	1.80	62.17	
SOI27	#1	S43	EDS	<	0.33	3.33	19.51	5.38		0.20	0.52	0.21	0.54	0.29	0.87	64.78	
<i>average</i>			<i>EDS</i>		<i>0.34</i>	<i>3.12</i>	<i>18.87</i>	<i>3.98</i>		<i>0.25</i>	<i>0.65</i>	<i>0.33</i>	<i>0.40</i>	<i>0.23</i>	<i>1.26</i>	<i>65.83</i>	

Table 16: Major element chemical composition of possible puddling slags.

		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO
YSF30	XRF	0.03	0.09	1.11	16.47	4.12	0.85	0.07	0.17	0.42	0.32	0.12	2.45	65.67
	average EDS	0.00	0.05	0.91	18.30	6.43	1.00	0.13	0.44	0.36	0.34	0.00	2.68	70.45
YSF31	XRF	0.02	0.02	0.82	16.83	4.12	0.87	0.08	0.18	0.42	0.30	0.09	2.45	66.49
	average EDS	0.06	0.04	1.01	18.03	6.72	1.10	0.14	0.52	0.31	0.22	0.00	2.75	68.65

Table 17: EDS Micro-analyses of the constituent minerals of possible puddling slags (1): phosphoran fayalite.

Sample	Area	Point	EDS in atomic%									formula (4 oxygens)					
			O	Mg	Al	Si	P	Ca	Mn	Fe	Si	P	Mg	Ca	Mn	Fe	Al
YSF30	SOI2	#7	56.86	<	0.22	13.59	0.62		1.25	27.46	0.96	0.04	<	<	0.09	1.93	0.02
YSF30	SOI5	#1	56.45		0.31	13.80	0.65		1.32	27.47	0.98	0.05	<	<	0.09	1.95	0.02
YSF30	SOI5	#2	56.38		0.37	13.67	0.66		1.18	27.74	0.97	0.05	<	<	0.08	1.97	0.03
YSF31	SOI 6	#7	58.22	<	0.19	13.13	0.68		1.31	26.46	0.90	0.05	<	<	0.09	1.82	0.01
YSF30	SOI2	#4	56.23		0.24	13.84	0.70		1.33	27.66	0.98	0.05	<	<	0.09	1.97	0.02
YSF30	SOI14	#1	55.37		0.21	14.20	0.70		1.38	28.14	1.03	0.05	<	<	0.10	2.03	0.01
YSF31	SOI 5	#1	58.45	<	0.24	12.84	0.83		1.32	26.33	0.88	0.06	<	<	0.09	1.80	0.02
YSF30	SOI11	#8	56.42	<	0.24	13.66	0.80		1.30	27.58	0.97	0.06	<	<	0.09	1.96	0.02
YSF30	SOI5	#3	55.89		0.21	13.64	0.96		1.27	28.04	0.98	0.07	<	<	0.09	2.01	0.02
YSF30	SOI11	#14	56.21		0.29	13.49	1.05		1.27	27.69	0.96	0.07	<	<	0.09	1.97	0.02
YSF30	SOI5	#4	56.75		0.32	13.19	1.14		1.23	27.37	0.93	0.08	<	<	0.09	1.93	0.02
YSF30	SOI11	#9	56.41		0.39	13.18	1.14		1.24	27.64	0.93	0.08	<	<	0.09	1.96	0.03
YSF30	SOI14	#11	55.55		0.38	13.29	1.40		1.28	28.09	0.96	0.10	<	<	0.09	2.02	0.03
YSF30	SOI11	#15	56.48		0.32	12.42	2.05		1.18	27.55	0.88	0.15	<	<	0.08	1.95	0.02
YSF30	SOI11	#10	56.91		0.28	11.74	2.74	0.06	1.22	27.04	0.83	0.19	<	<	0.09	1.90	0.02
YSF30	SOI5	#5	56.77		0.31	10.96	3.69	0.06	1.35	26.85	0.77	0.26	<	<	0.10	1.89	0.02
YSF30	SOI2	#3	57.02	<	0.31	10.46	4.18	0.08	1.28	26.68	0.73	0.29	<	0.01	0.09	1.87	0.02
YSF30	SOI11	#16	56.89	0.15	0.31	10.16	4.52		1.26	26.69	0.71	0.32	0.01	<	0.09	1.88	0.02
YSF30	SOI2	#5	57.58		0.26	9.25	5.60	0.08	1.36	25.86	0.64	0.39	<	0.01	0.09	1.80	0.02
YSF30	SOI5	#6	57.60		0.40	8.94	5.82	<	1.29	25.95	0.62	0.40	<	<	0.09	1.80	0.03
YSF30	SOI7	#2	57.49		0.30	8.74	6.10		1.31	26.05	0.61	0.42	<	<	0.09	1.81	0.02
YSF30	SOI7	#1	57.89		0.24	8.39	6.47		1.37	25.63	0.58	0.45	<	<	0.09	1.77	0.02
YSF30	SOI7	#3	58.10		0.31	7.56	7.41		1.41	25.22	0.52	0.51	<	<	0.10	1.74	0.02
YSF30	SOI2	#2	58.03		0.24	7.05	7.97	0.08	1.50	25.13	0.49	0.55	<	0.01	0.10	1.73	0.02
YSF30	SOI11	#11	58.02		0.28	7.01	8.04	0.09	1.35	25.21	0.48	0.55	<	0.01	0.09	1.74	0.02
YSF30	SOI5	#7	58.78		0.24	5.60	9.48	0.08	1.46	24.36	0.38	0.65	<	0.01	0.10	1.66	0.02
YSF31	SOI 5	#12	60.51		0.22	4.46	9.99	0.14	1.40	23.28	0.29	0.66	<	0.01	0.09	1.54	0.01
YSF31	SOI 5	#18	61.04	<	0.21	4.54	10.14	0.09	1.36	22.62	0.30	0.66	<	0.01	0.09	1.48	0.01
YSF30	SOI11	#17	58.20		0.26	5.50	9.85	0.11	1.50	24.58	0.38	0.68	<	0.01	0.10	1.69	0.02
YSF31	SOI 5	#11	61.12	<	0.15	4.04	10.43	0.12	1.54	22.20	0.26	0.68	<	0.01	0.10	1.45	0.01
YSF30	SOI11	#12	59.24		0.27	4.77	10.44	0.10	1.42	23.76	0.32	0.70	<	0.01	0.10	1.60	0.02
YSF30	SOI5	#13	58.98		0.11	4.52	10.94	0.13	1.47	23.86	0.31	0.74	<	0.01	0.10	1.62	0.01
YSF30	SOI11	#18	58.71		0.30	4.41	10.94	0.13	1.37	24.15	0.30	0.75	<	0.01	0.09	1.65	0.02

Table 18: EDS Micro-analyses of the constituent minerals of possible puddling slags (2): alkali-bearing phosphate.

Sample	Area	Point	EDS in atomic%										formula (8 oxygens)						
			O	Na	Al	Si	P	K	Ca	Ti	Mn	Fe	Si	P	Ca	Mn	Fe	Al	Na+K
YSF31	SOI 5	#14	60.11	1.42	0.00	0.72	14.16	2.62	2.69	0.00	1.61	16.69	0.10	1.88	0.36	0.21	2.22	0.00	0.54
YSF31	SOI 5	#19	61.11	1.44	0.14	0.69	13.94	2.95	2.49	0.00	1.58	15.66	0.09	1.83	0.33	0.21	2.05	0.02	0.57

Table 19: EDS Micro-analyses of the constituent minerals of possible puddling slags (3): iron-calcium-manganese phosphates.

Sample	Area	Point	EDS in atomic%							formula (8 oxygens)					
			O	Al	Si	P	Ca	Mn	Fe	Si	P	Ca	Mn	Fe	Al
YSF30	SOI5	#12	60.68	<	0.63	14.99	4.46	1.89	17.36	0.08	1.98	0.59	0.25	2.29	<
YSF30	SOI11	#13	60.18	0.11	0.61	15.25	3.94	1.85	18.06	0.08	2.03	0.52	0.25	2.40	0.01
YSF30	SOI11	#19	60.34	0.11	0.66	15.05	3.85	1.84	18.15	0.09	2.00	0.51	0.24	2.41	0.01
YSF30	SOI11	#24	60.23	<	0.44	15.39	4.00	1.79	18.16	0.06	2.04	0.53	0.24	2.41	<
YSF30	SOI11	#25	60.18	<	0.62	15.05	3.88	1.92	18.34	0.08	2.00	0.52	0.25	2.44	<
YSF30	SOI11	#27	60.08	<	0.37	15.38	3.84	1.96	18.35	0.05	2.05	0.51	0.26	2.44	<
YSF30	SOI14	#4	59.67	0.10	0.57	15.47	3.23	2.16	18.81	0.08	2.07	0.43	0.29	2.52	0.01

Table 20: EDS Micro-analyses of the constituent minerals of possible puddling slags (4): phosphoran iscorite.

Sample	Area	Point	EDS in atomic%								formula (10 oxygens)							
			O	Al	Si	P	Ti	V	Mn	Fe	Si	P	Mn	Fe ²⁺	Al	Fe ³⁺	Ti	V
YSF31	SOI8	#15	52.13	0.38	4.56	0.74	0.26	0.16	0.77	41.01	0.88	0.14	0.15	4.85	0.07	3.02	0.05	0.03
YSF30	SOI5	#11	53.84	2.39	4.40	0.80	0.89	0.21	0.48	37.00	0.82	0.15	0.09	4.91	0.44	1.96	0.17	0.04
YSF31	SOI 5	#4	55.01	1.93	4.02	1.12	0.63	0.17	0.50	36.60	0.73	0.20	0.09	4.91	0.35	1.74	0.12	0.03
YSF31	SOI 5	#3	54.49	1.34	3.19	1.17	0.30	0.19	0.45	38.88	0.58	0.21	0.08	4.92	0.25	2.22	0.05	0.04
YSF30	SOI14	#15	52.48	0.92	2.94	1.73	0.24	0.24	0.60	40.85	0.56	0.33	0.11	4.89	0.18	2.90	0.05	0.04
YSF30	SOI6	#2	53.05	1.99	3.12	1.83	0.30	<	0.44	39.27	0.59	0.34	0.08	4.92	0.37	2.49	0.06	<
YSF30	SOI11	#20	53.04	1.63	3.62	1.97	0.69	0.11	0.46	38.50	0.68	0.37	0.09	4.91	0.31	2.35	0.13	0.02
YSF30	SOI14	#5	52.14	0.91	2.77	2.06	0.25	0.16	0.51	41.20	0.53	0.39	0.10	4.90	0.17	3.00	0.05	0.03
YSF30	SOI11	#21	53.52	1.28	3.30	2.34	0.72	<	0.54	38.30	0.62	0.44	0.10	4.90	0.24	2.26	0.13	<
YSF30	SOI5	#18	52.78	0.81	2.22	2.36	0.29	<	0.53	41.00	0.42	0.45	0.10	4.90	0.15	2.87	0.06	<
YSF30	SOI6	#8	53.39	1.32	2.25	2.69	0.20	<	0.57	39.58	0.42	0.50	0.11	4.89	0.25	2.52	0.04	<

Table 21: Major element chemical composition of acid Bessemer convertor slags

			Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO
YSF6		XRF	0.01	0.05	2.13	55.83	0.07	0.14	0.30	<0.004	1.02	0.09	0.03	19.35	20.97
SOI5	#5	EDS	0.20		1.89	72.98		<	0.13		0.75			13.56	12.96
SOI7	#5	EDS		0.16	1.99	77.45		<	0.25	<	0.65			9.79	13.36
SOI10	#1	EDS	<		2.28	67.51		<	0.14		0.92			16.24	15.56
	<i>average</i>	<i>EDS</i>			<i>2.05</i>	<i>72.65</i>			<i>0.18</i>		<i>0.77</i>			<i>13.19</i>	<i>13.96</i>
YSF7		XRF	<	0.05	1.67	59.73	0.02	0.21	0.23	<0.004	1.00	0.07	0.02	12.68	24.32
SOI2	#1	EDS			1.58	68.09		<	0.00	0.14	1.22			14.83	18.79
SOI3	#2	EDS	<	<	2.63	80.19		<	0.64		0.82			7.74	10.83
	<i>average</i>	<i>EDS</i>			<i>2.10</i>	<i>74.14</i>			<i>0.32</i>		<i>1.02</i>			<i>11.29</i>	<i>14.81</i>

Table 22: EDS Micro-analyses of the constituent minerals of acid Bessemer convertor slags

				EDS in atomic%										formula (oxygen as shown)								Si+Al	Mg+Ca+Ti +Mn+Fe
				O	Mg	Al	Si	K	Ca	Ti	Mn	Fe	O	Mg	Al	Si	K	Ca	Ti	Mn	Fe		
YSF6	SOI6	#3	porous	59.23	<	0.93	18.06	0.15		0.28	11.04	10.31	3.00	<	0.05	0.91	0.01	<	0.01	0.56	0.52	0.96	1.10
YSF6	SOI6	#6	porous	59.05		1.64	19.02	0.19	0.09	0.39	1<	9.62	3.00	<	0.08	0.97	0.01	<	0.02	0.51	0.49	1.05	1.02
YSF6	SOI6	#4	porous	59.61		1.24	18.72	0.21		0.31	10.22	9.69	3.00	<	0.06	0.94	0.01	<	0.02	0.51	0.49	1.00	1.02
YSF6	SOI9	#5	porous	58.76	0.15	1.22	17.95	0.28		0.22	11.05	10.36	3.00	0.01	0.06	0.92	0.01	<	0.01	0.56	0.53	0.98	1.11
YSF6	SOI9	#4	porous	58.70	0.16	0.92	17.18	0.22		0.24	11.68	10.89	3.00	0.01	0.05	0.88	0.01	<	0.01	0.60	0.56	0.93	1.17
YSF7	SOI1	#8	porous	57.23	<	0.50	18.12	0.14		0.18	10.79	13.04	3.00	<	0.03	0.95	0.01	<	0.01	0.57	0.68	0.98	1.26
YSF7	SOI1	#9	porous	56.90	0.14	0.44	18.21	0.12		0.17	10.85	13.18	3.00	0.01	0.02	0.96	0.01	<	0.01	0.57	0.69	0.98	1.28
YSF7	SOI1	#11	porous	57.00	<	0.49	17.70	0.21		0.12	11.01	13.47	3.00	<	0.03	0.93	0.01	<	0.01	0.58	0.71	0.96	1.30
YSF7	SOI1	#10	porous	56.91		0.49	17.84	0.20		0.10	11.05	13.41	3.00	<	0.03	0.94	0.01	<	0.01	0.58	0.71	0.97	1.29
YSF6	SOI9	#3	solid	58.01	0.15	0.28	14.84	0.07		0.08	13.67	12.92	4.00	0.01	0.02	1.02	<	<	0.01	0.94	0.89	1.04	1.85
YSF6	SOI9	#8	solid	57.77	0.19	0.35	15.66	0.07			13.41	12.55	4.00	0.01	0.02	1.08	<	<	<	0.93	0.87	1.11	1.81
YSF6	SOI9	#2	solid	57.81	<	0.52	16.00	0.09		0.13	13.22	12.24	4.00	<	0.04	1.11	0.01	<	0.01	0.91	0.85	1.14	1.77
YSF7	SOI1	#3	solid	56.01		0.21	15.61			0.09	12.71	15.37	4.00	<	0.02	1.11	<	<	0.01	0.91	1.10	1.13	2.01
YSF7	SOI1	#6	solid	56.06	<	0.19	15.71			0.12	12.63	15.29	4.00	<	0.01	1.12	<	<	0.01	0.90	1.09	1.13	2.00
YSF7	SOI1	#2	solid	55.96		0.34	15.88			0.15	12.55	15.12	4.00	<	0.02	1.14	<	<	0.01	0.90	1.08	1.16	1.99

Table 23: Major element chemical composition of clinker

YSF1	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Mn ₃ O ₄	FeO
XRF	0.33	1.83	23.59	56.02	0.15	0.09	5.25	0.25	1.03	0.04	0.02	0.19	9.57
average EDS	0.45	1.75	25.21	56.14	0.05	0.03	5.15	0.60	1.05	0.00	0.00	0.06	8.22

Figure 1

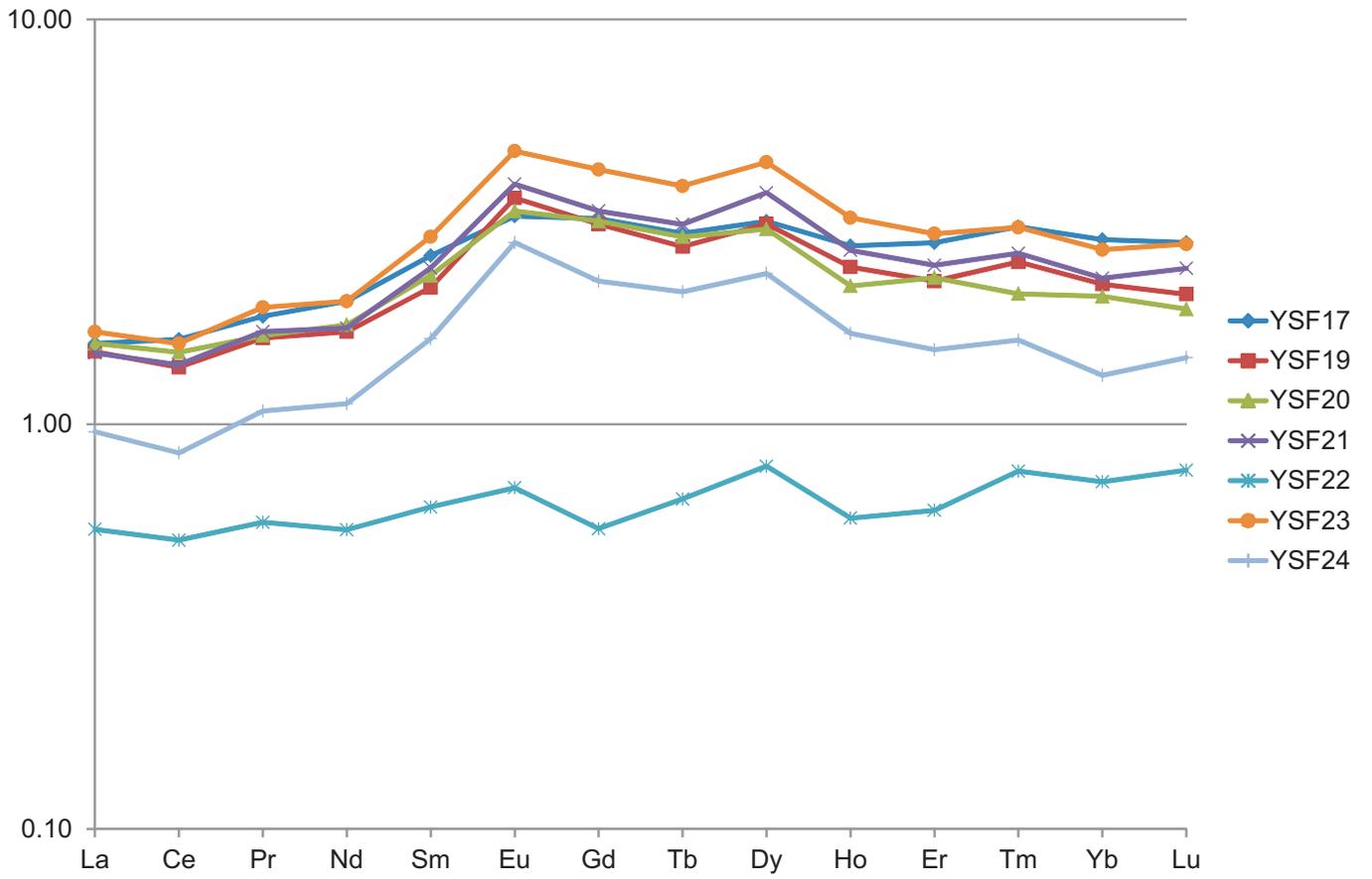


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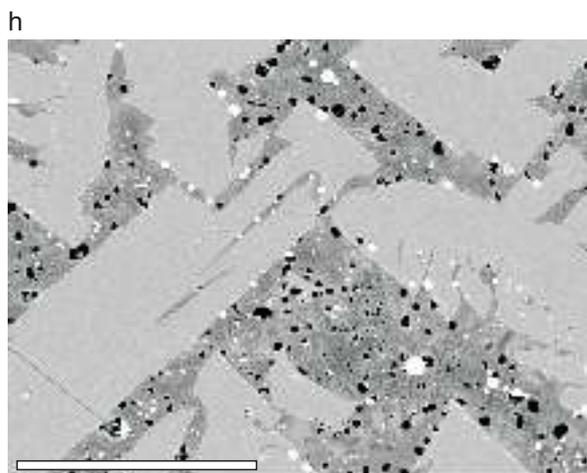
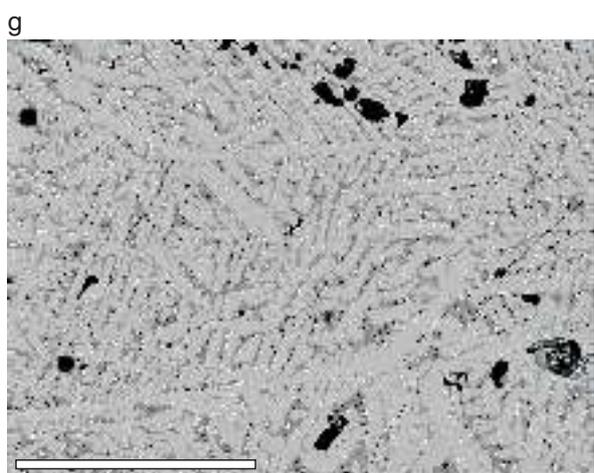
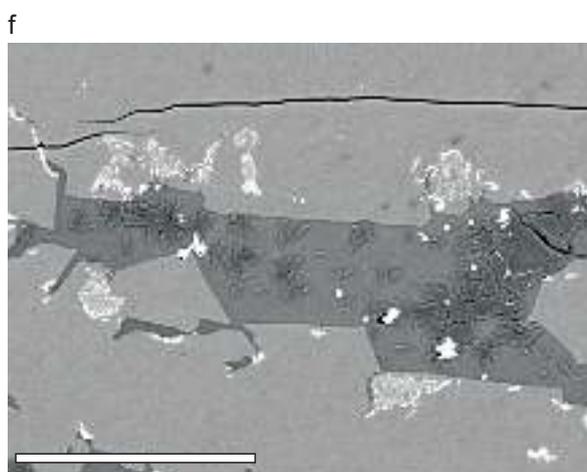
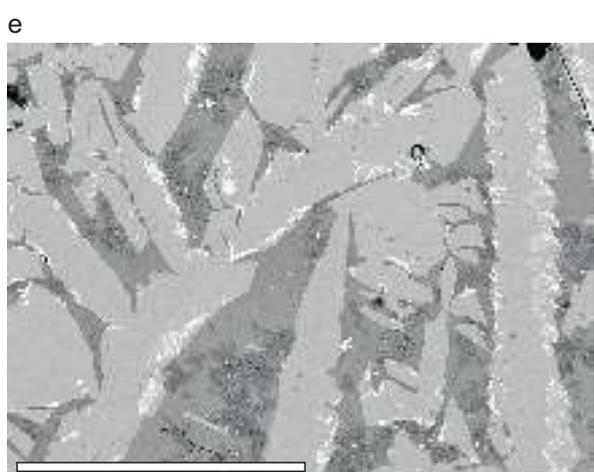
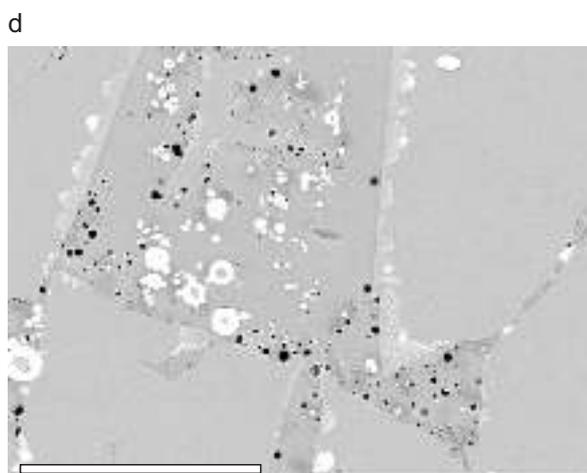
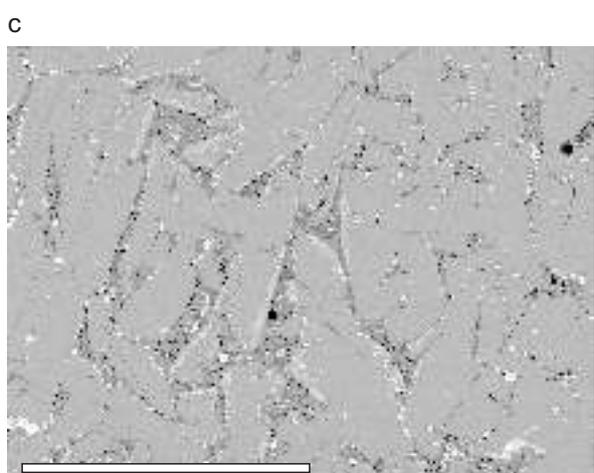
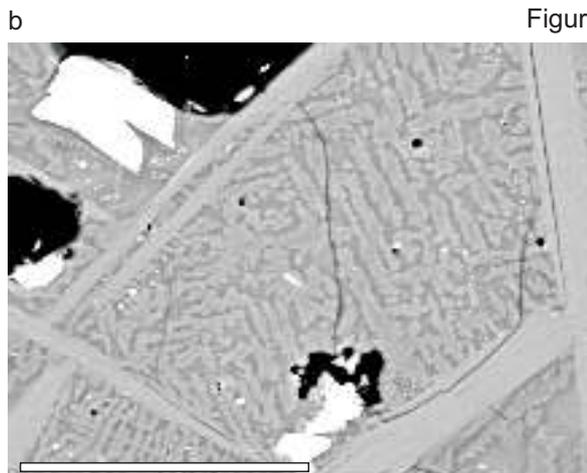
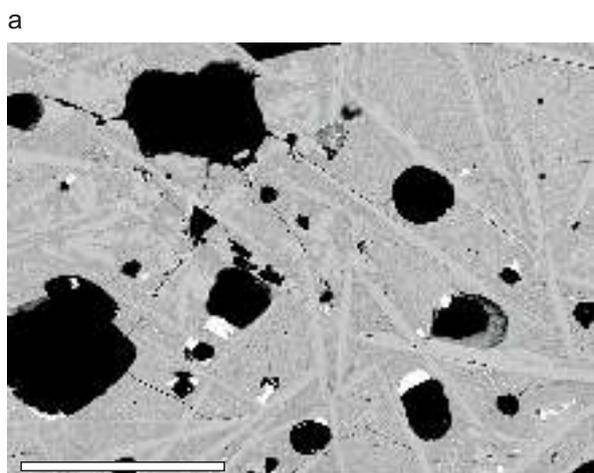


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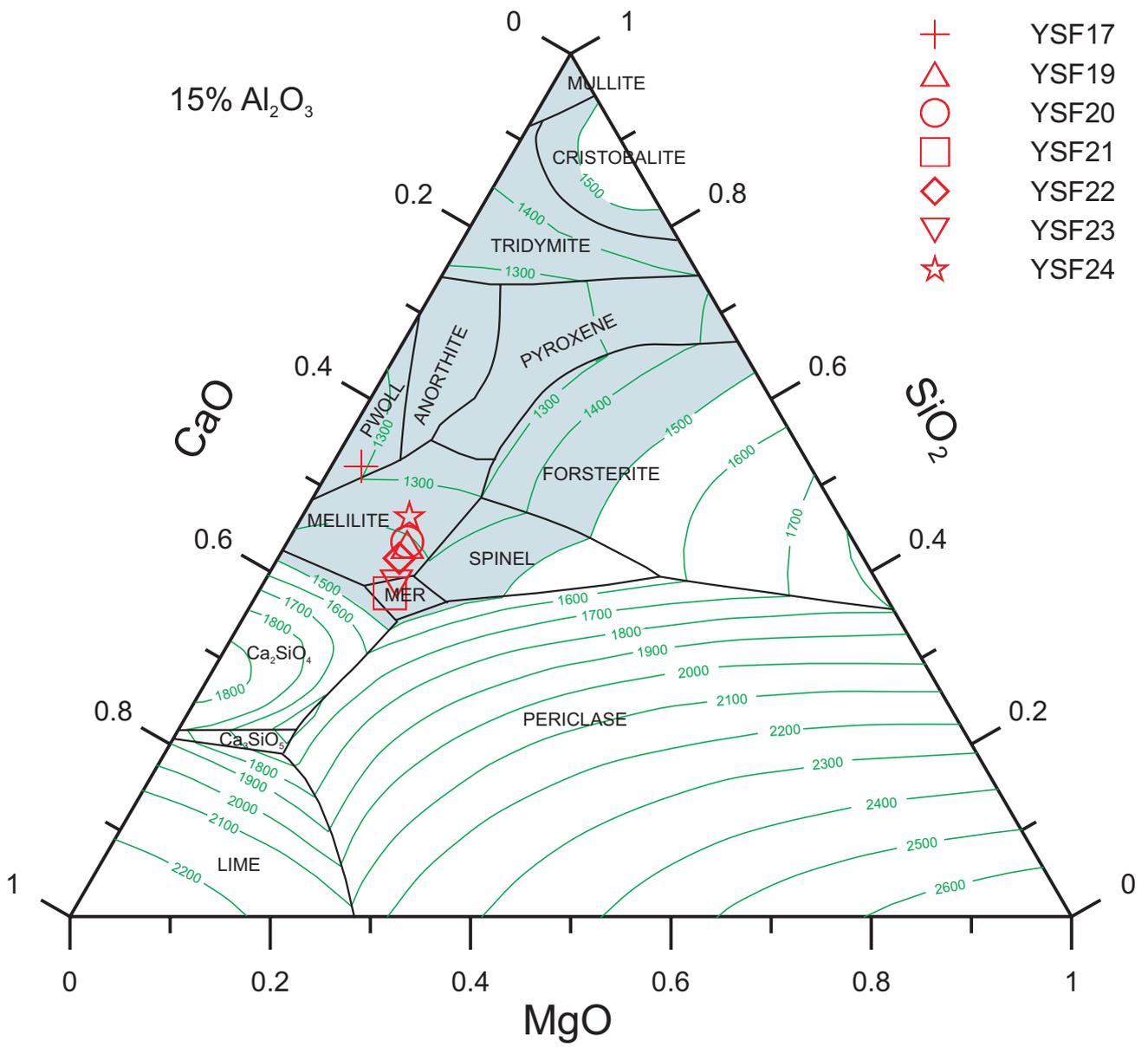


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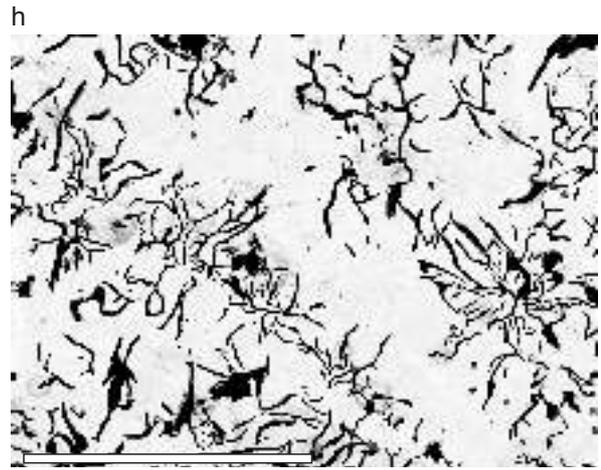
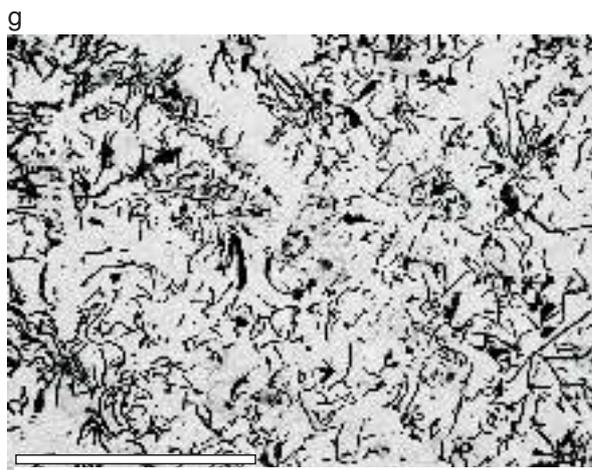
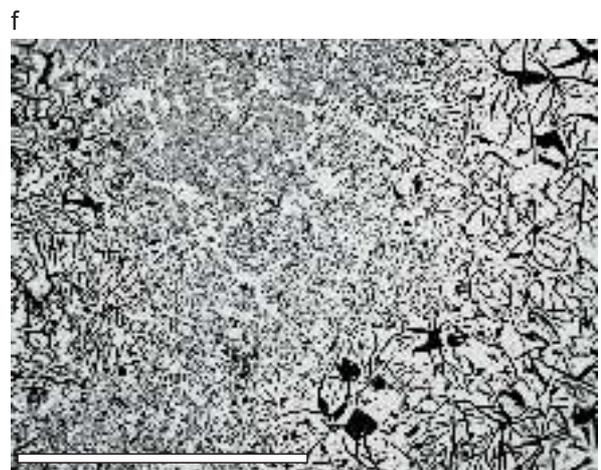
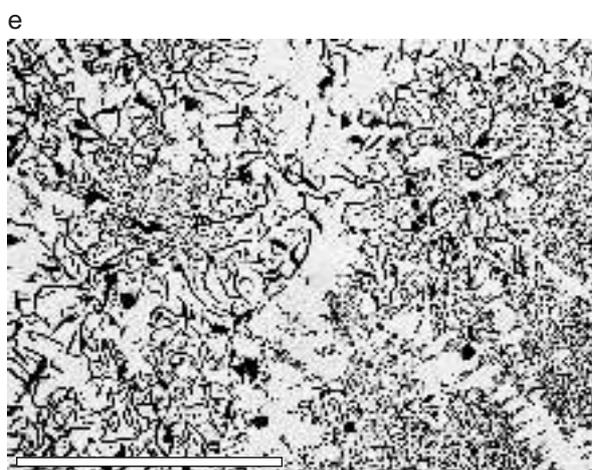
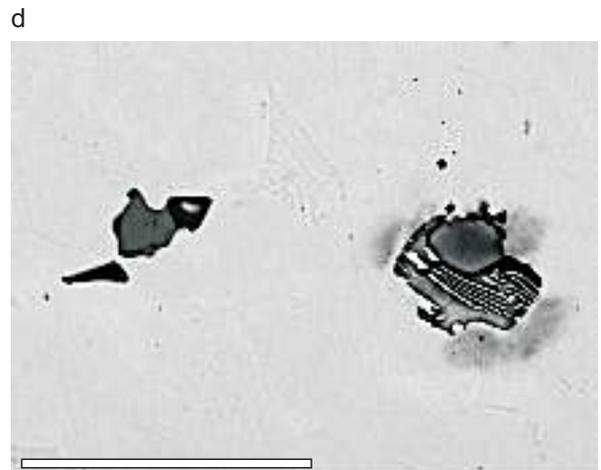
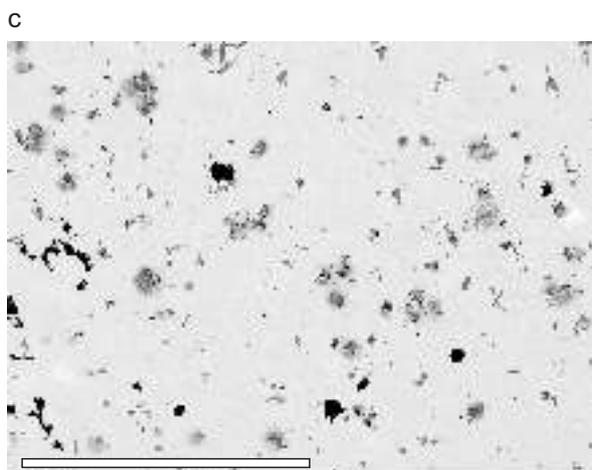
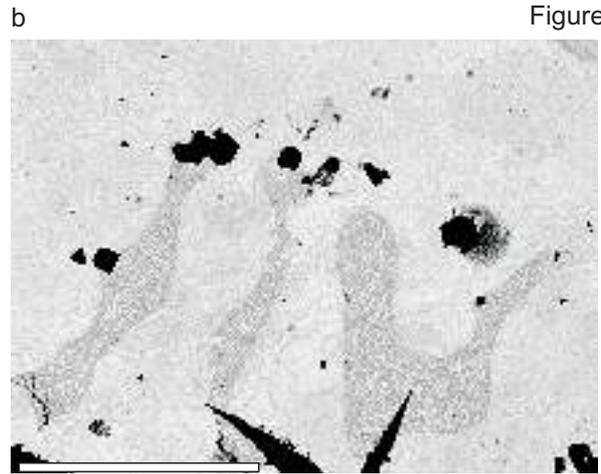


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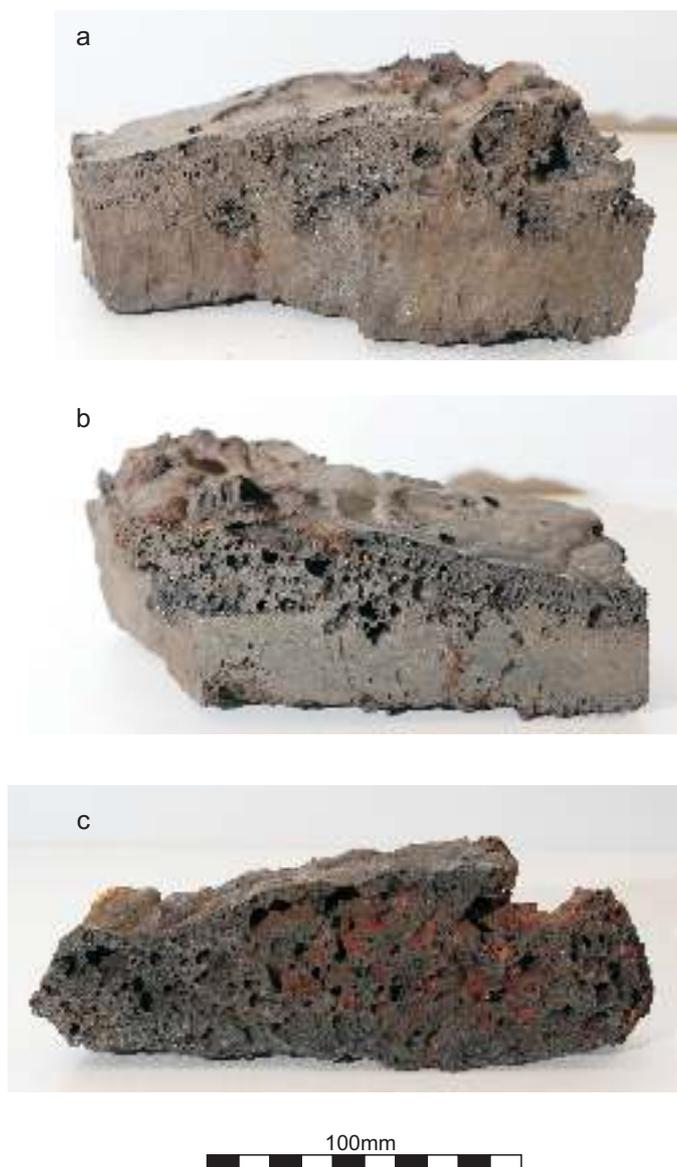


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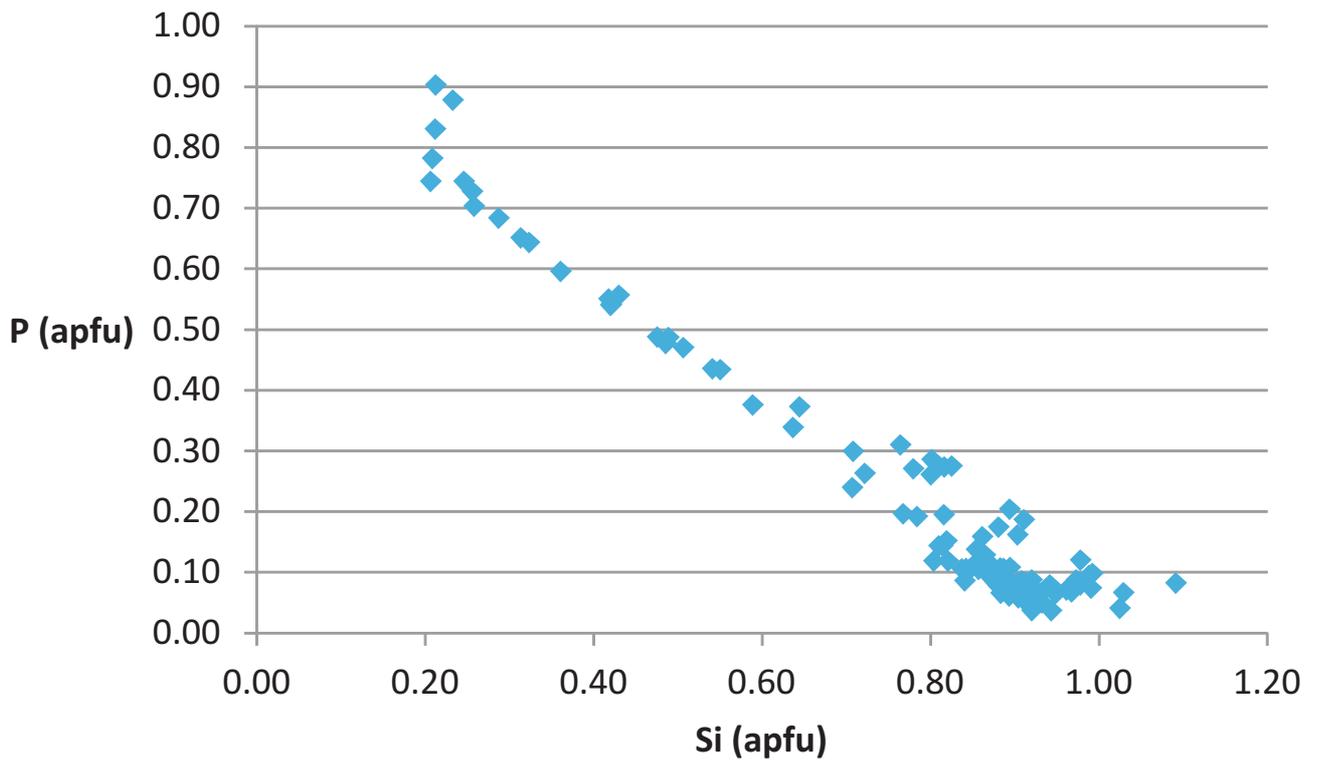


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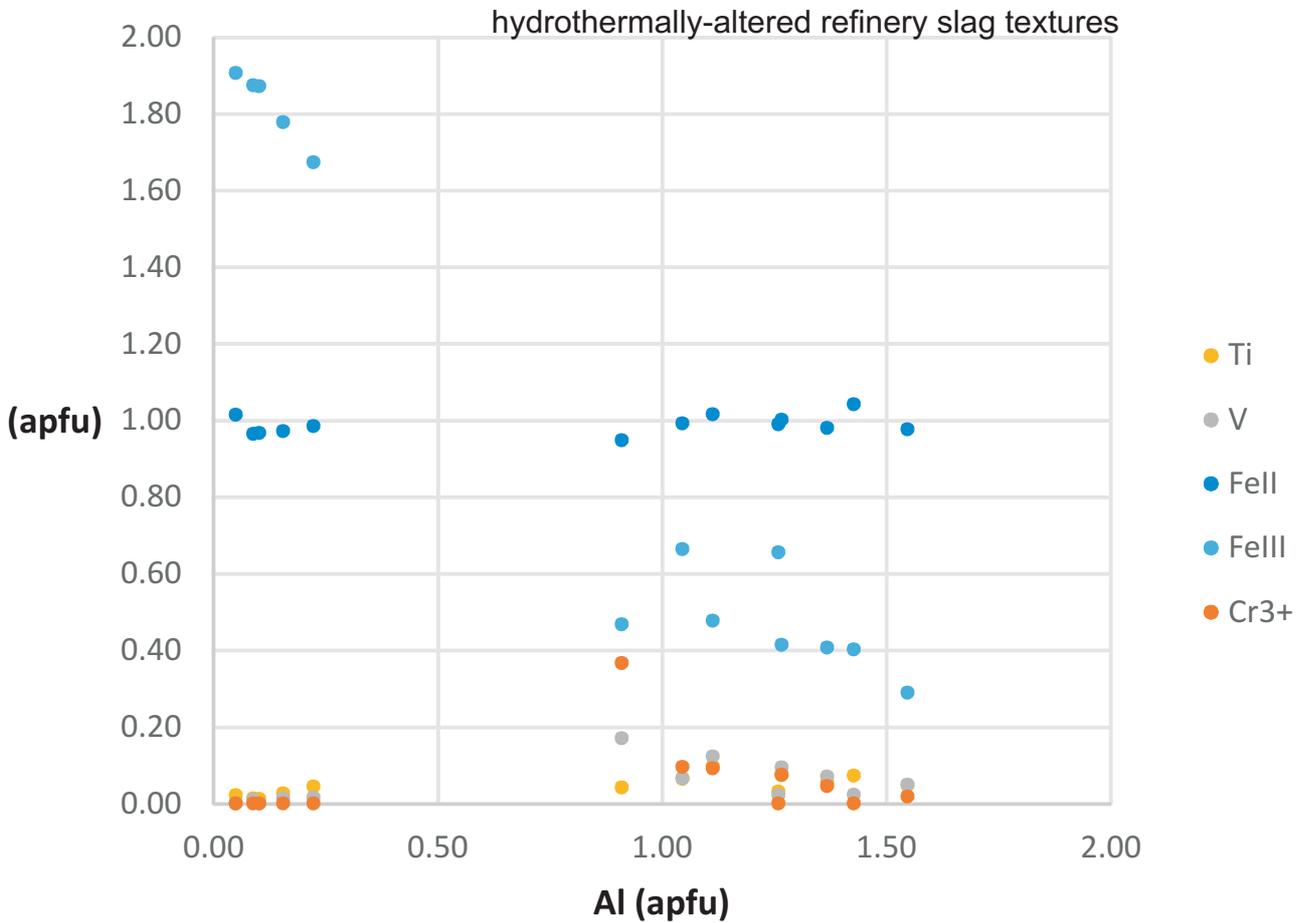
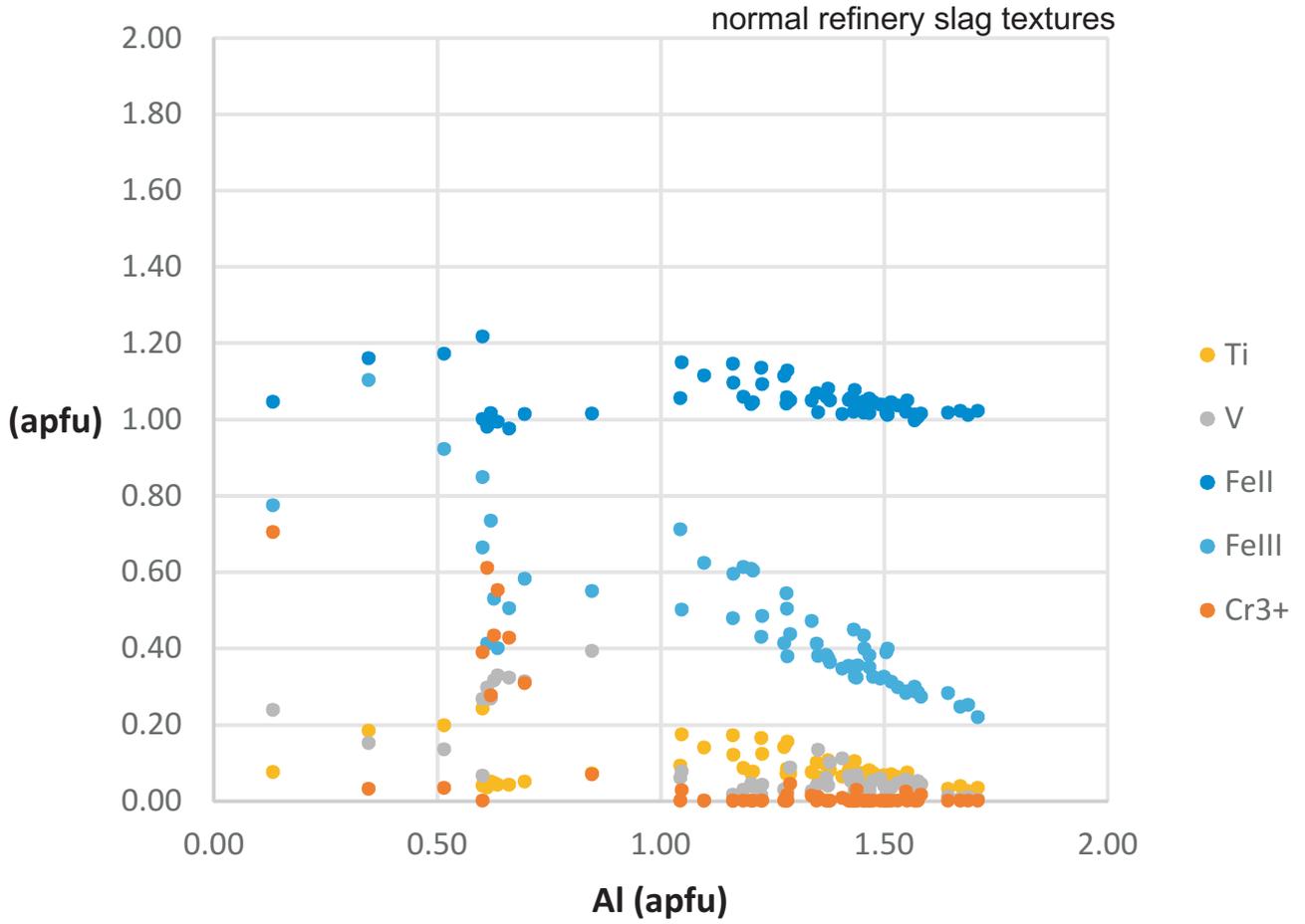


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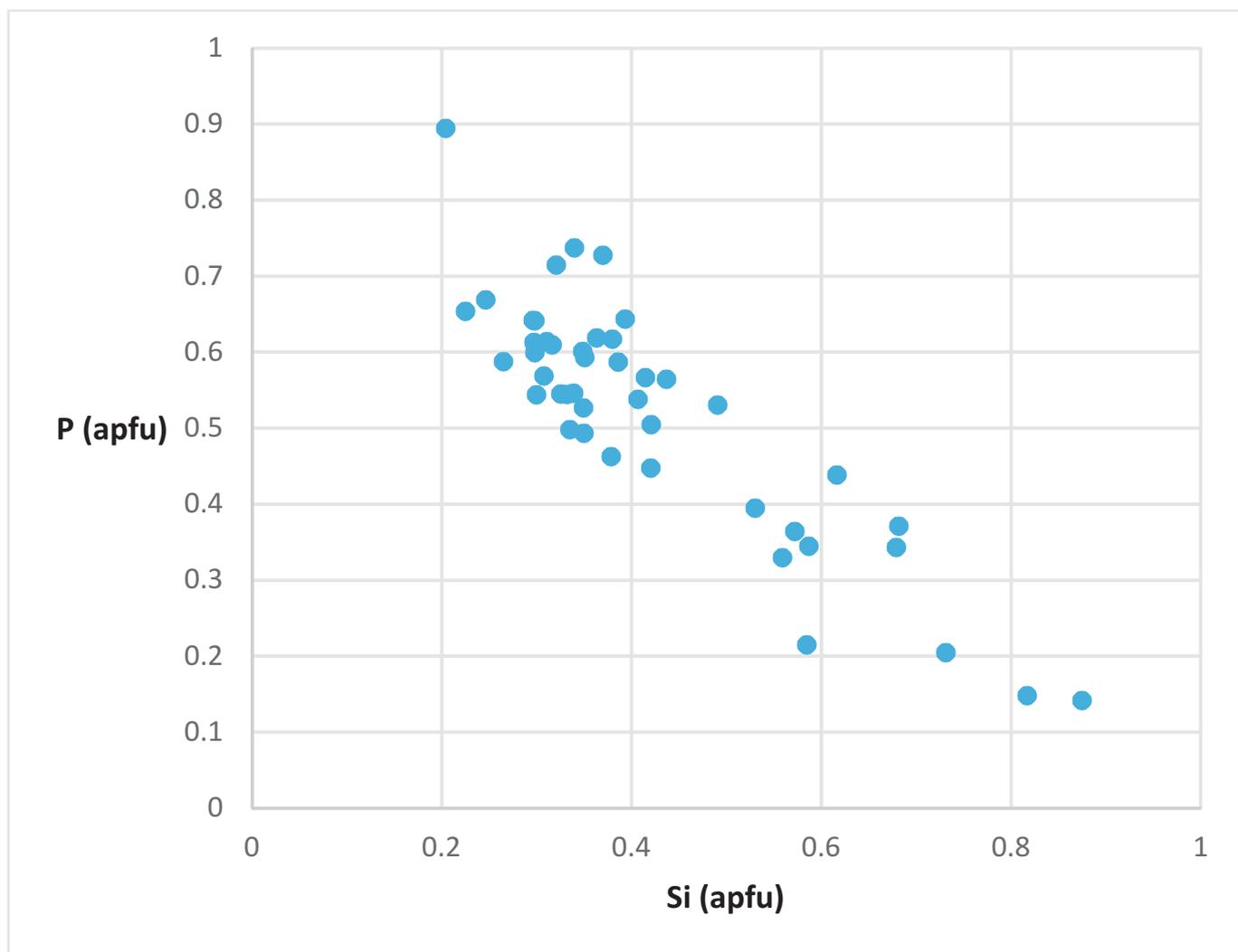


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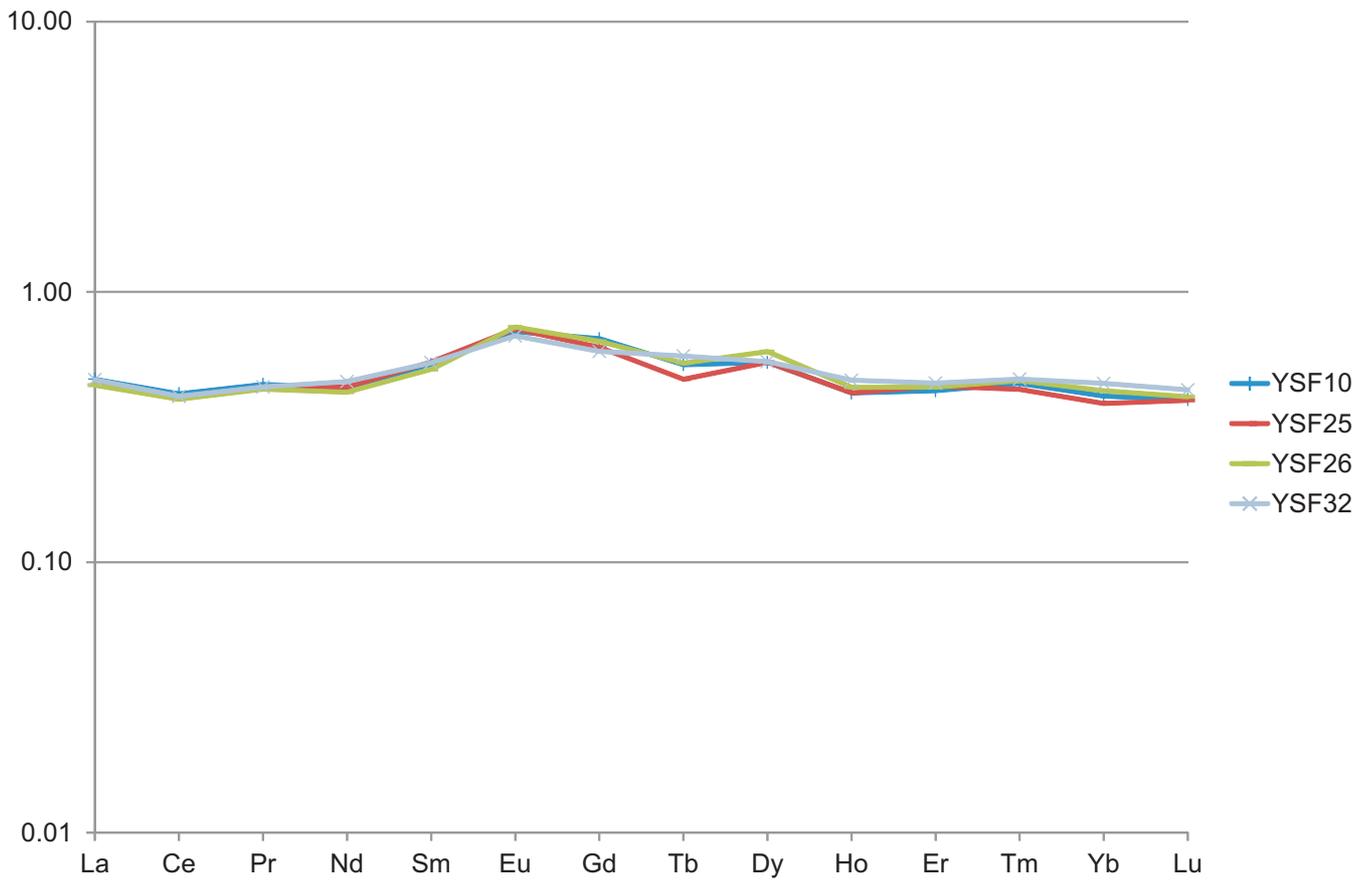
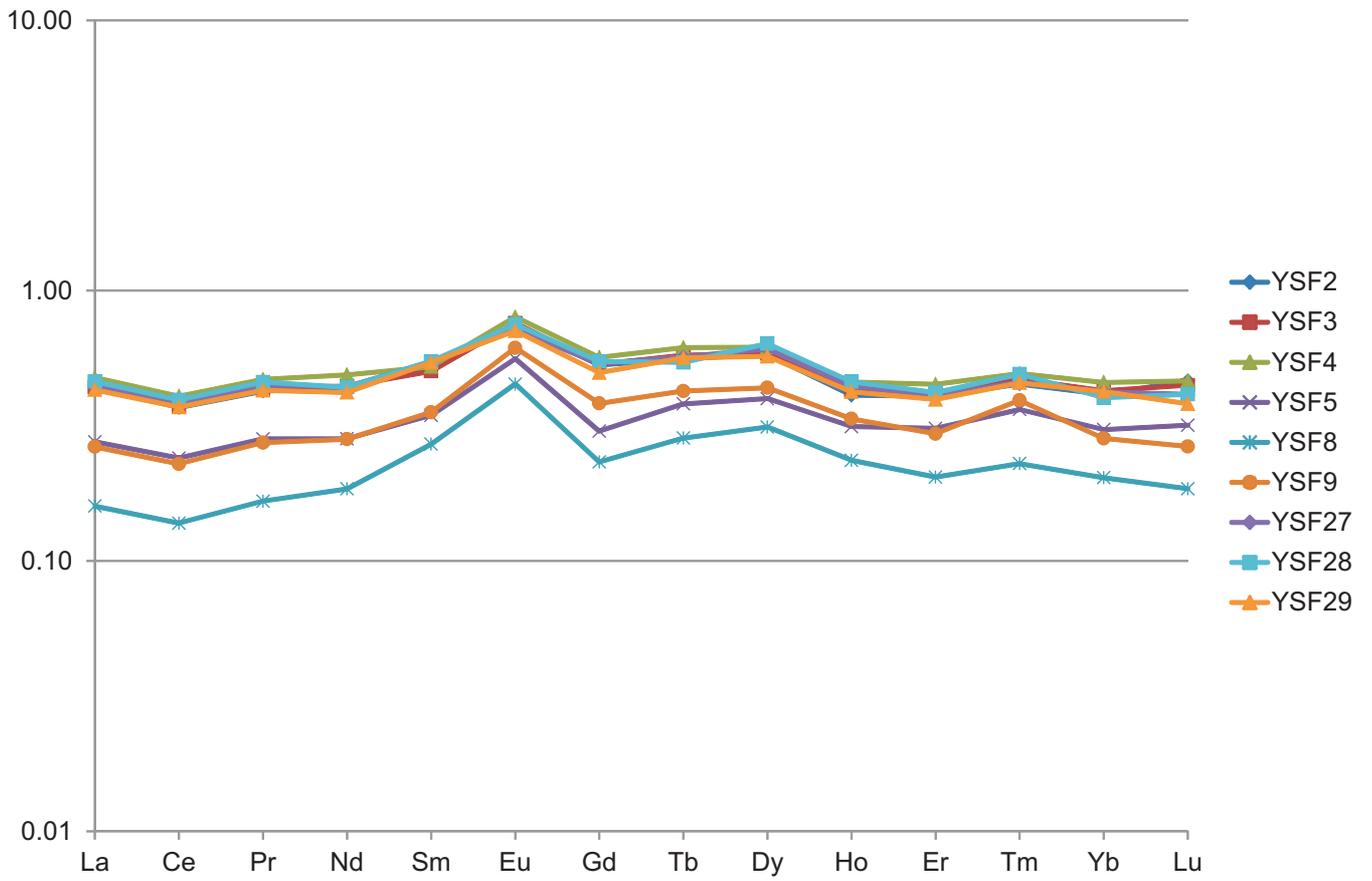


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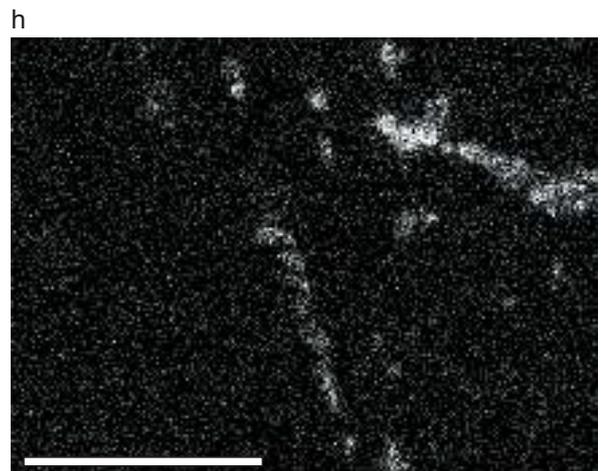
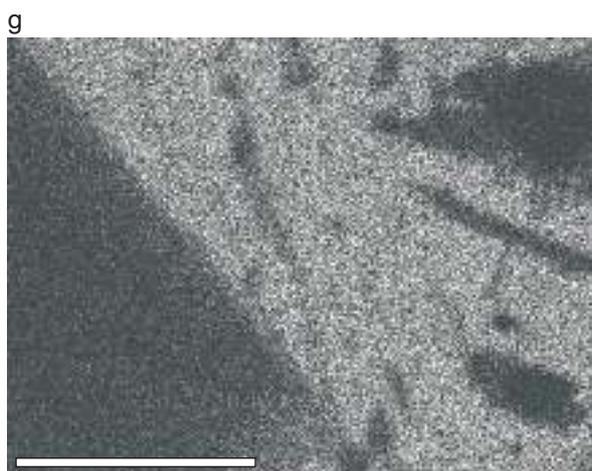
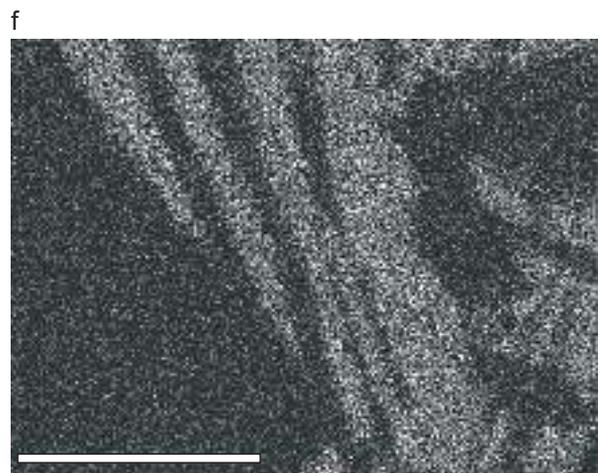
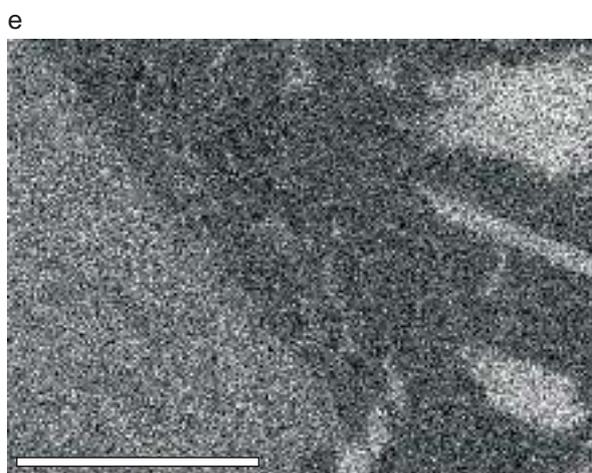
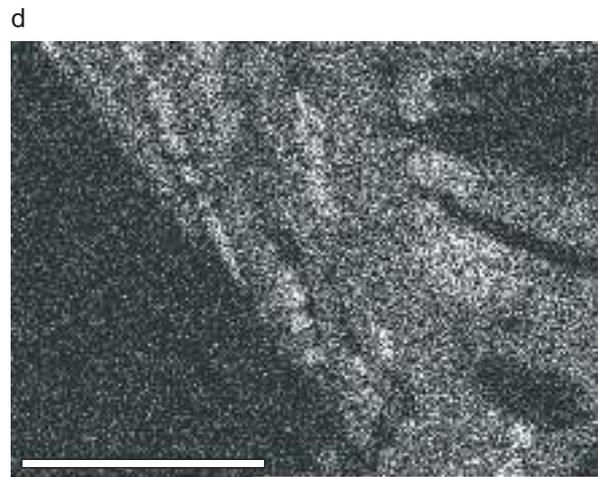
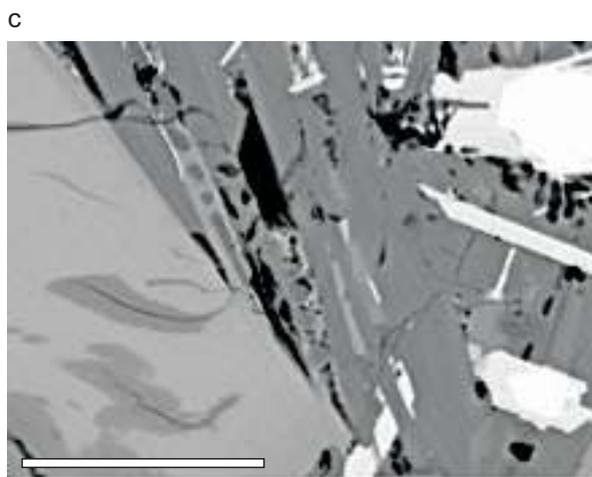
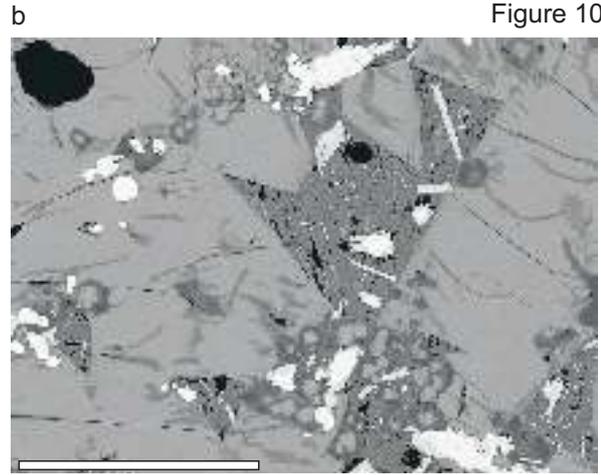
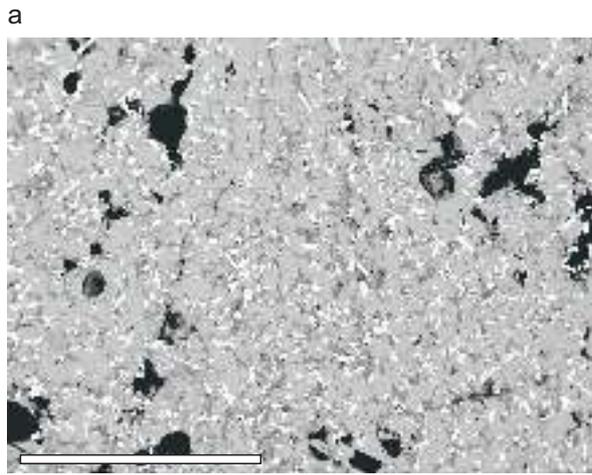


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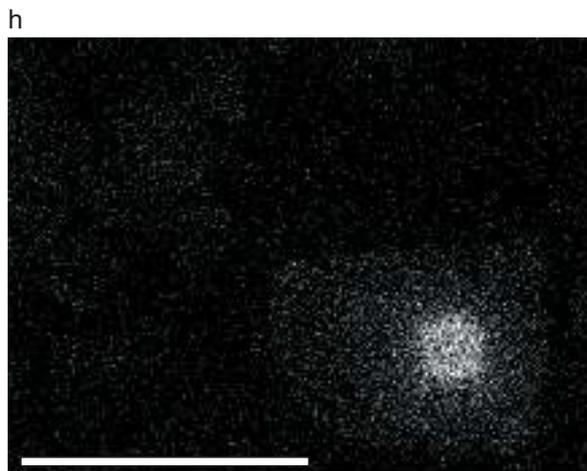
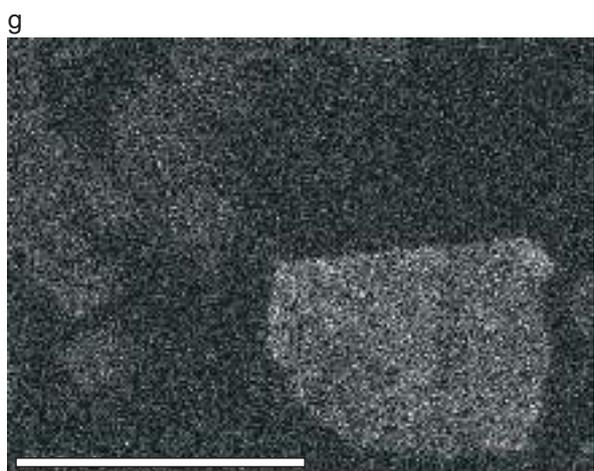
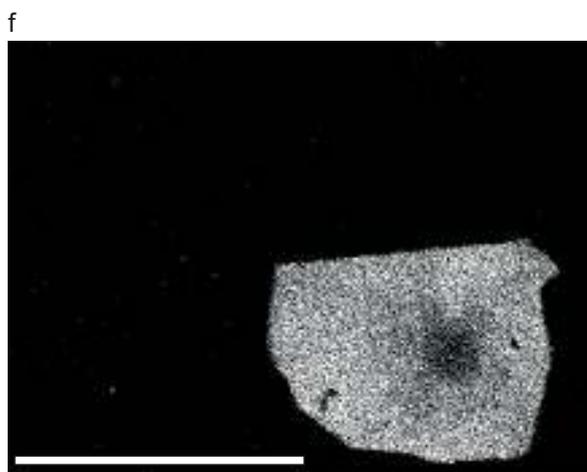
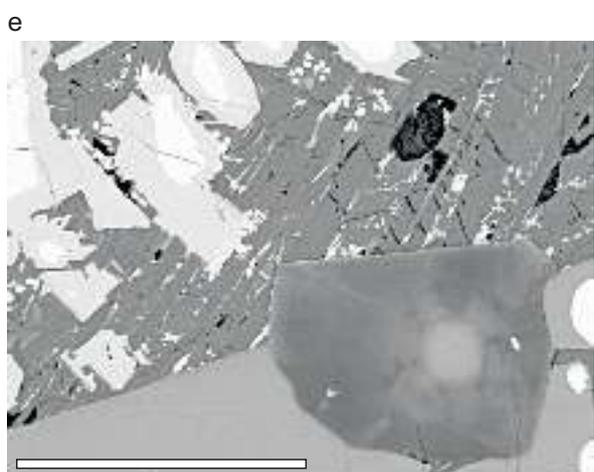
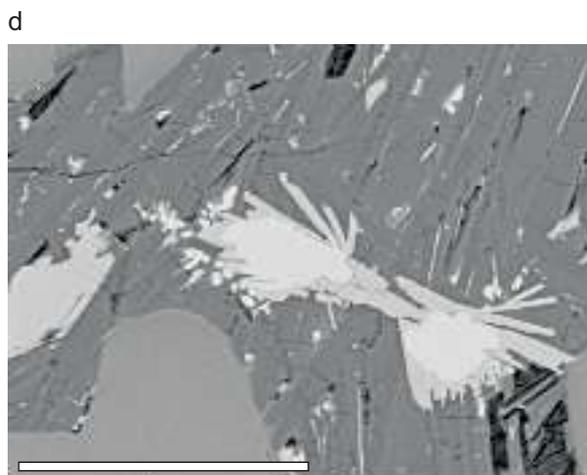
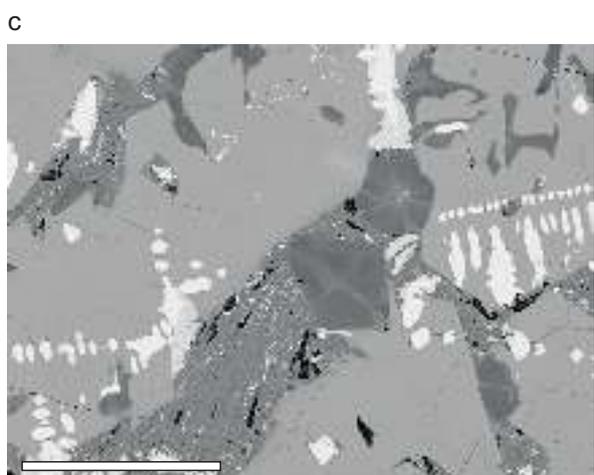
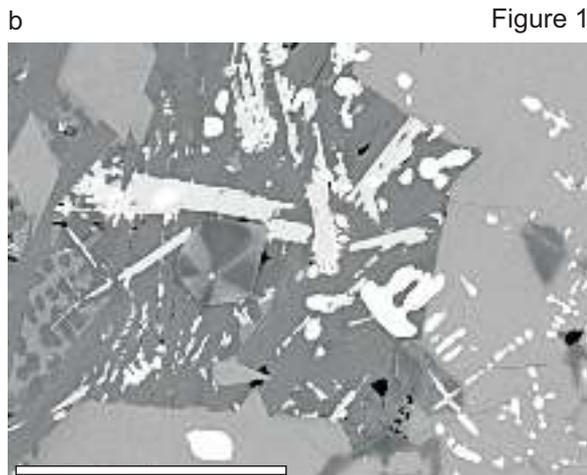
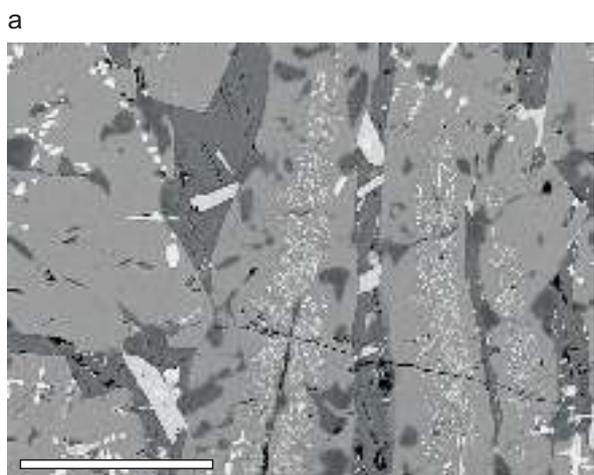
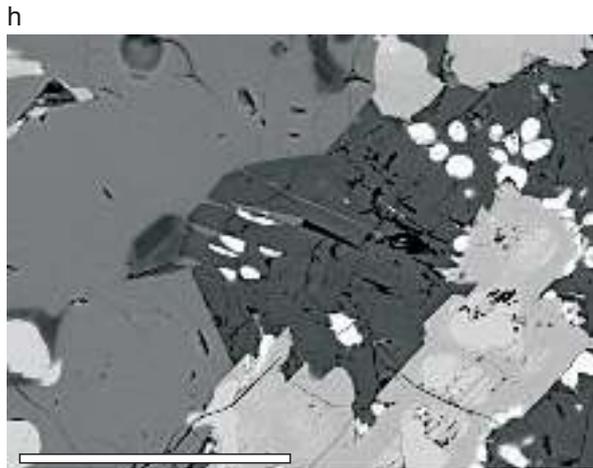
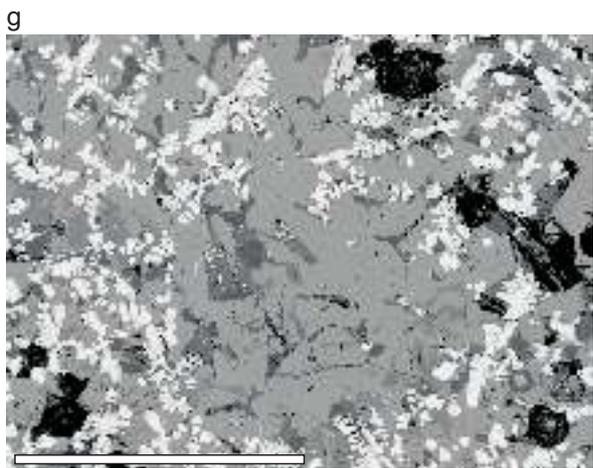
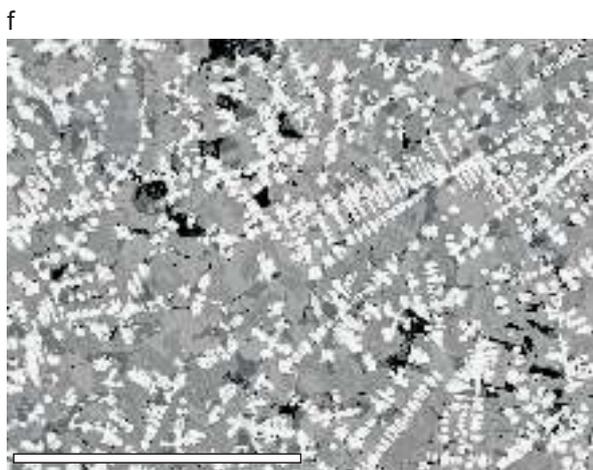
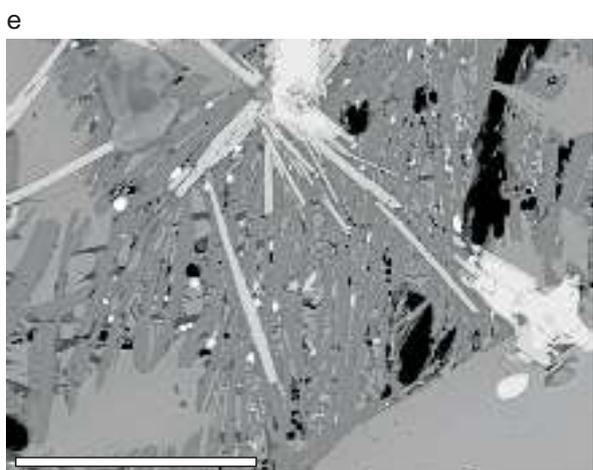
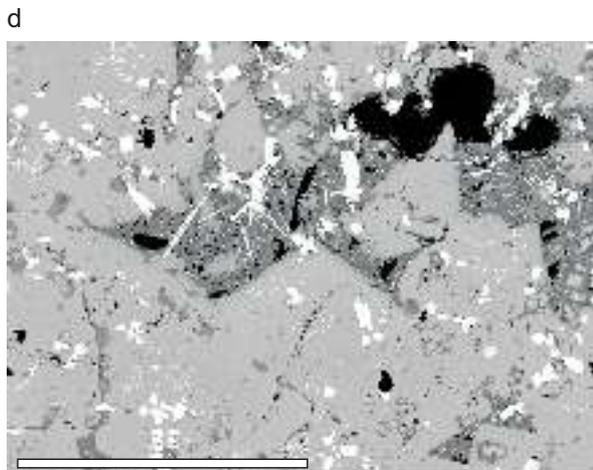
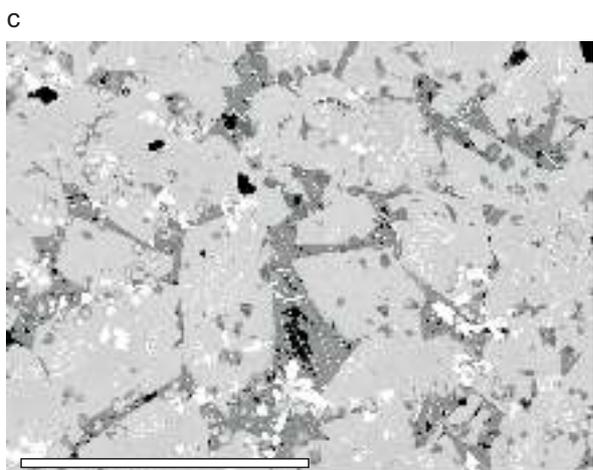
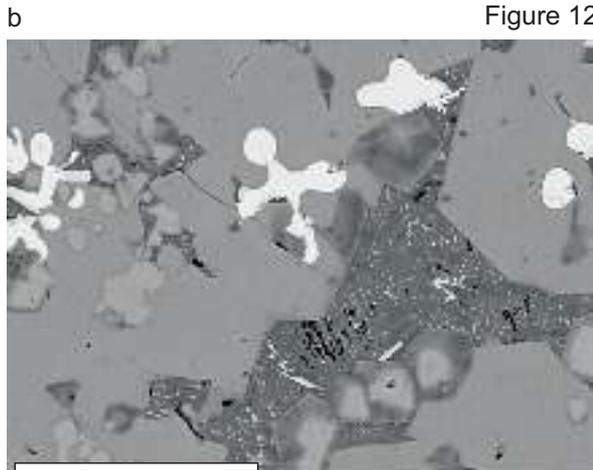
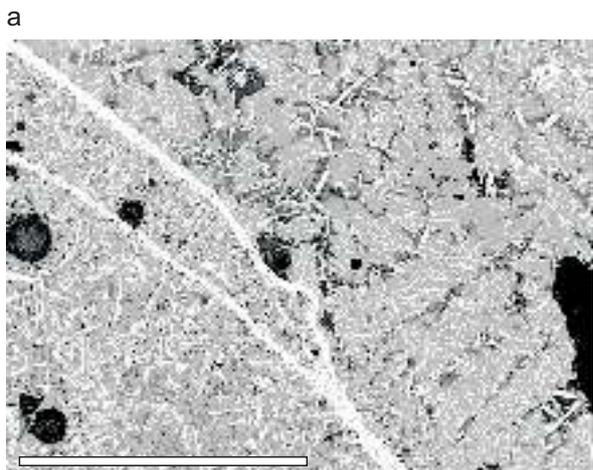


Figure 12



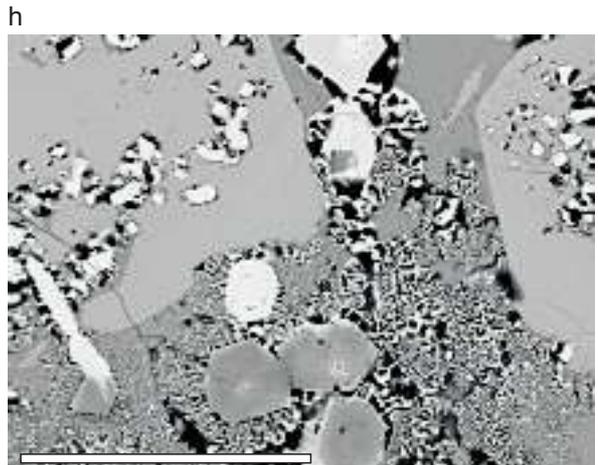
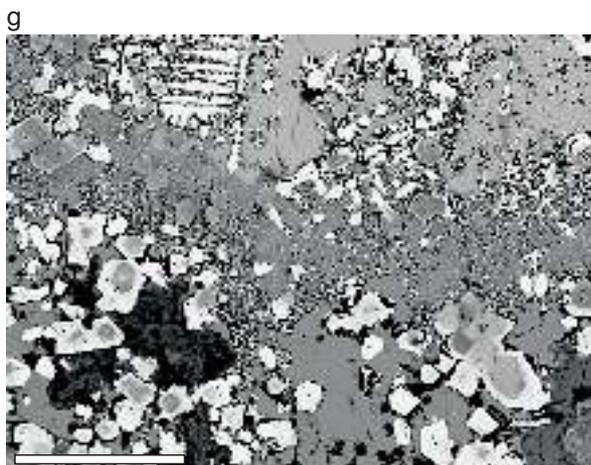
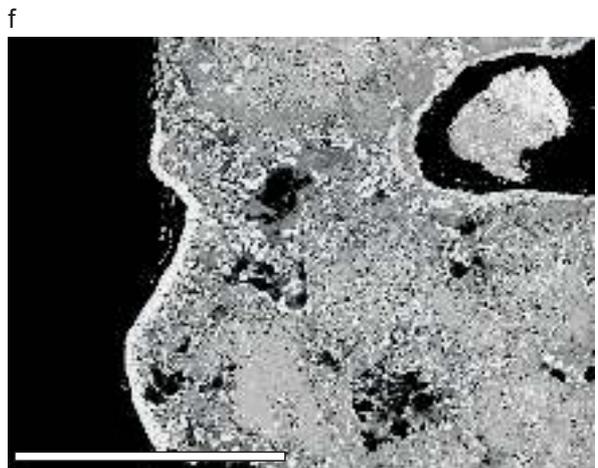
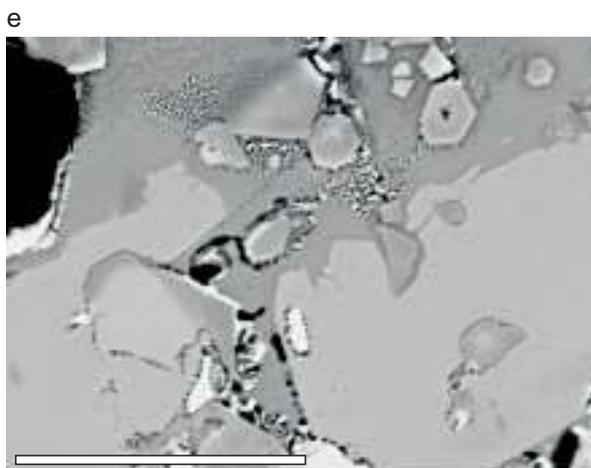
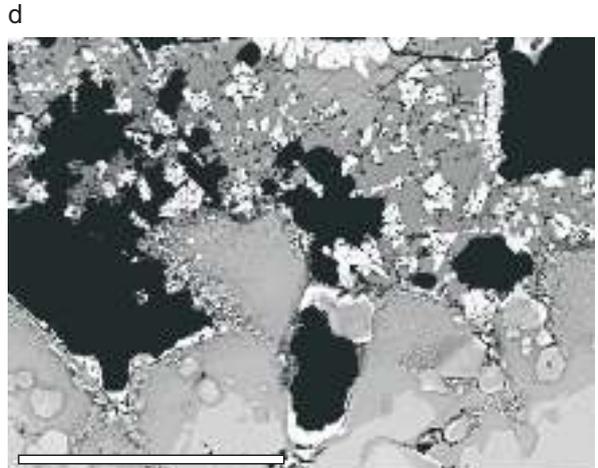
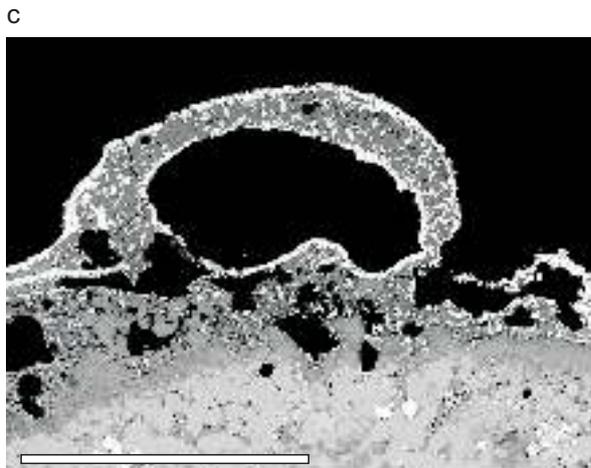
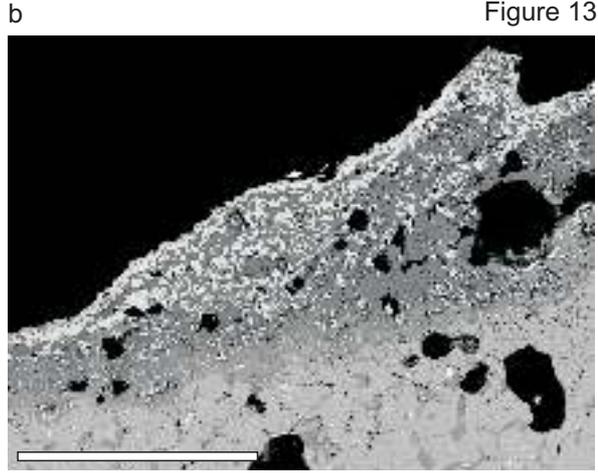
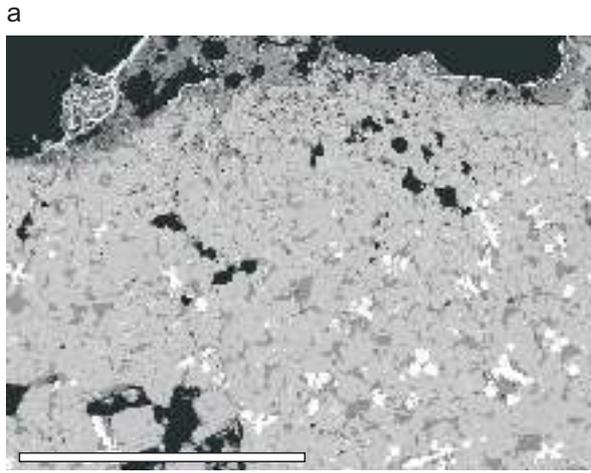


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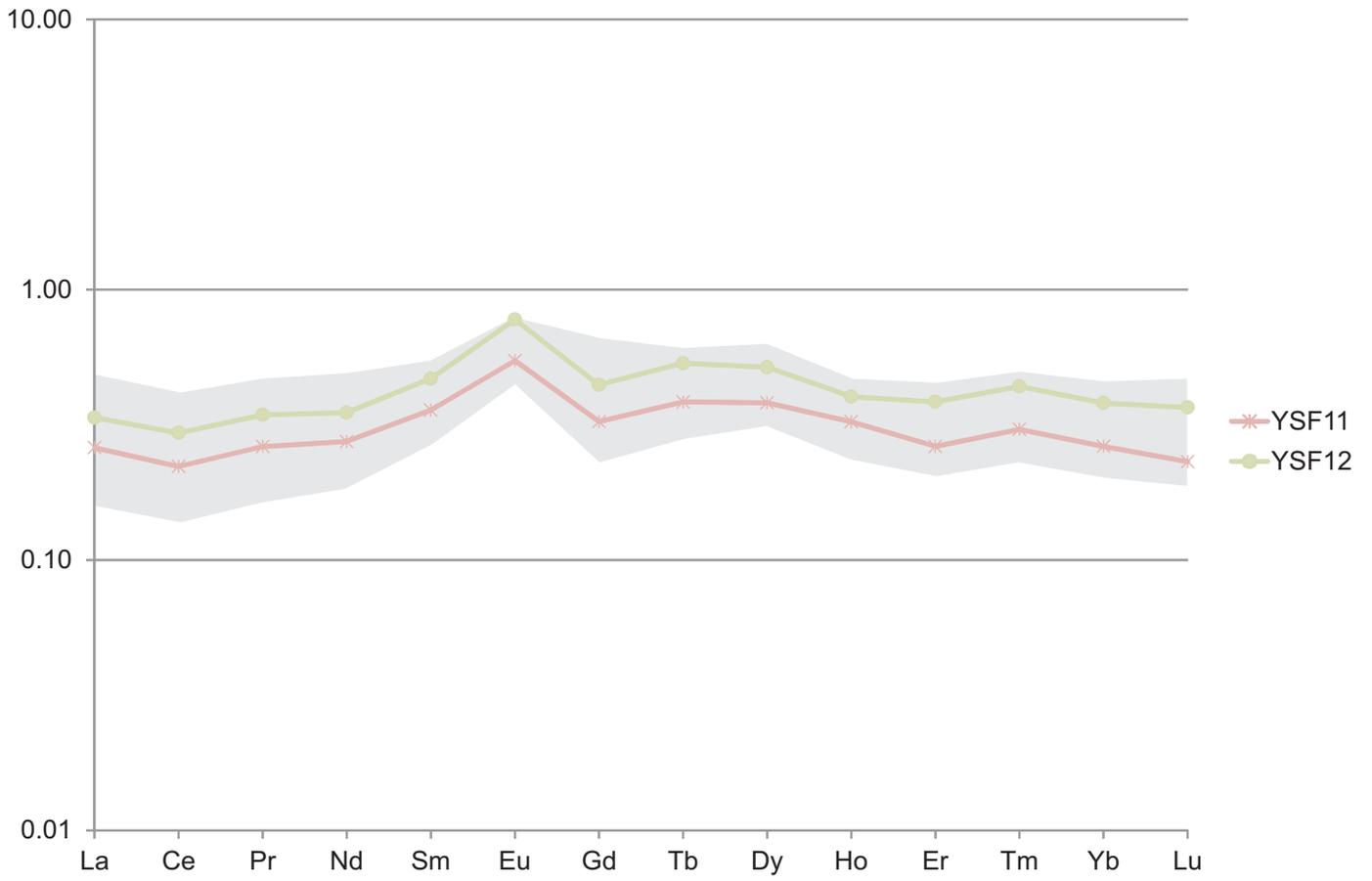


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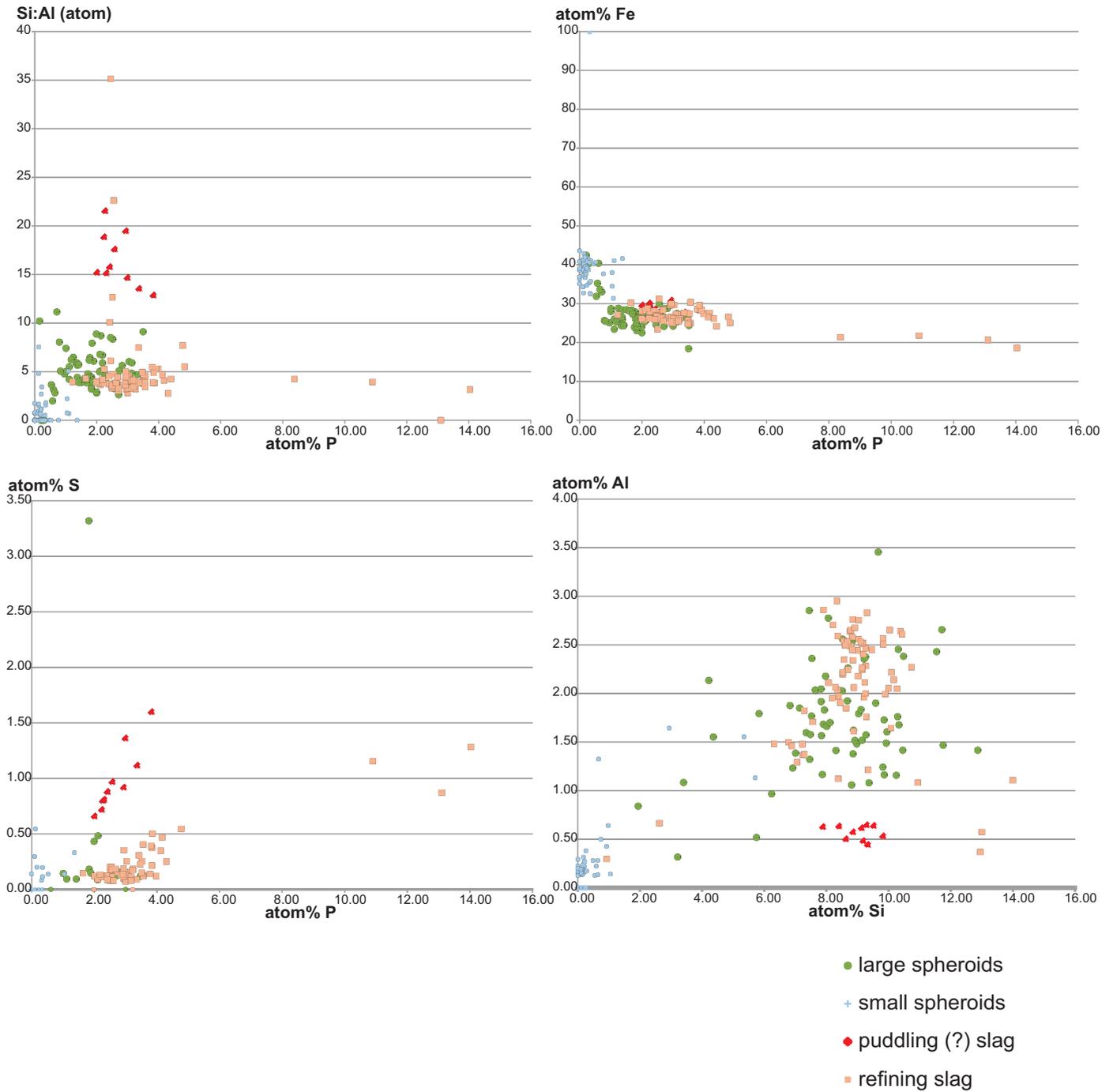
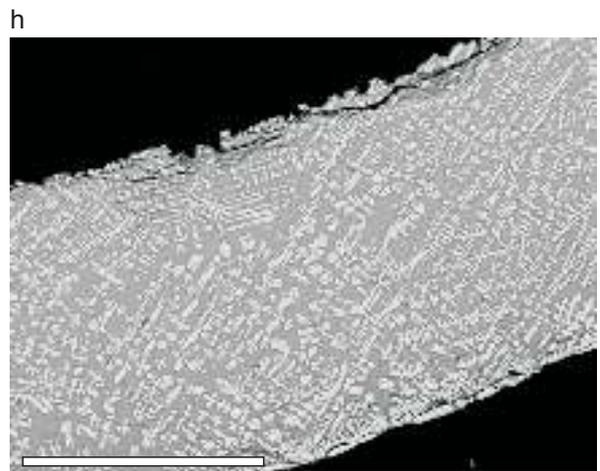
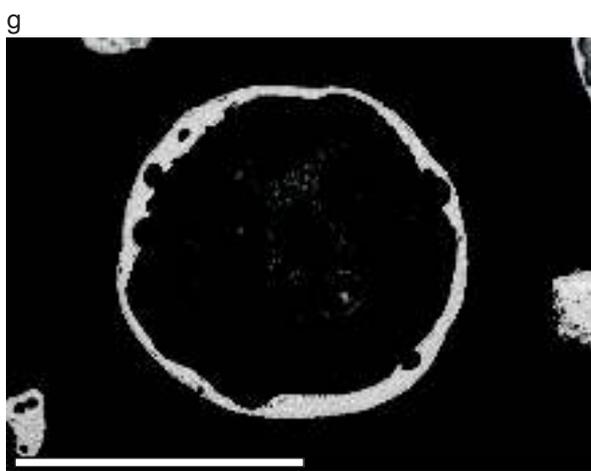
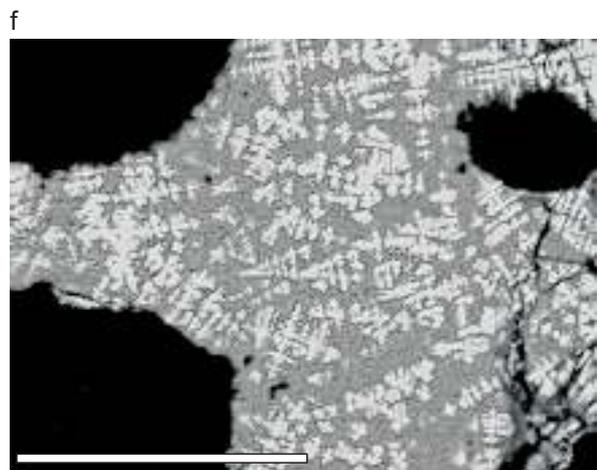
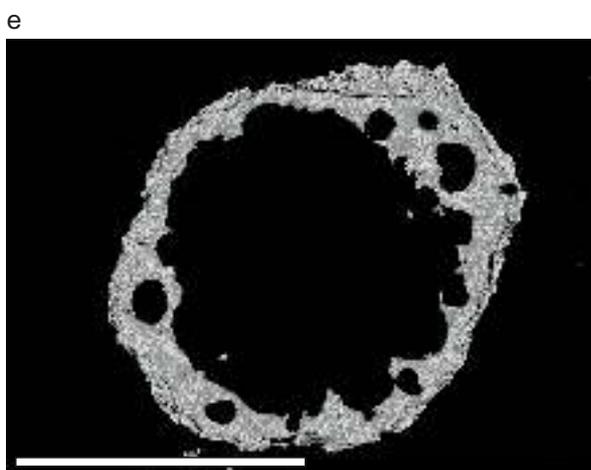
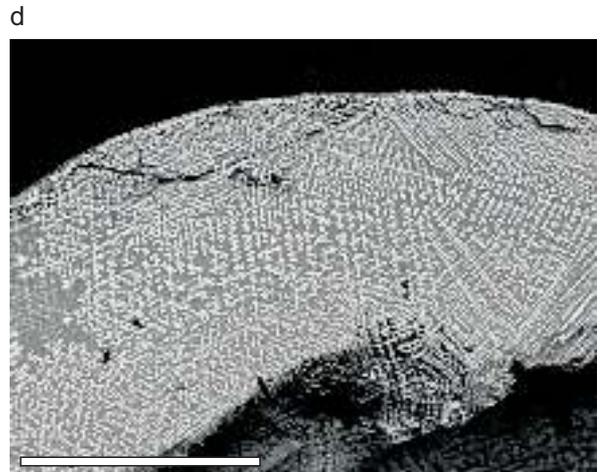
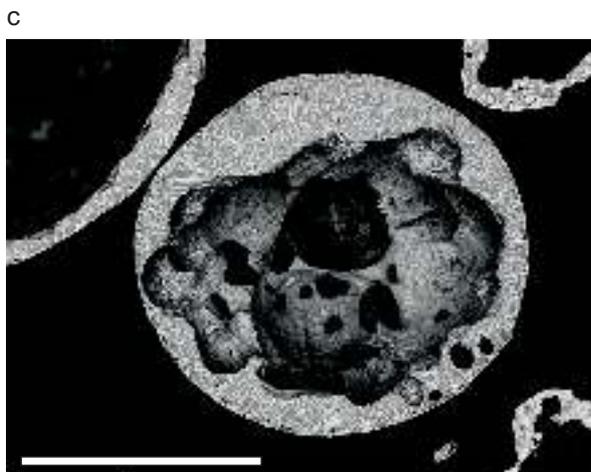
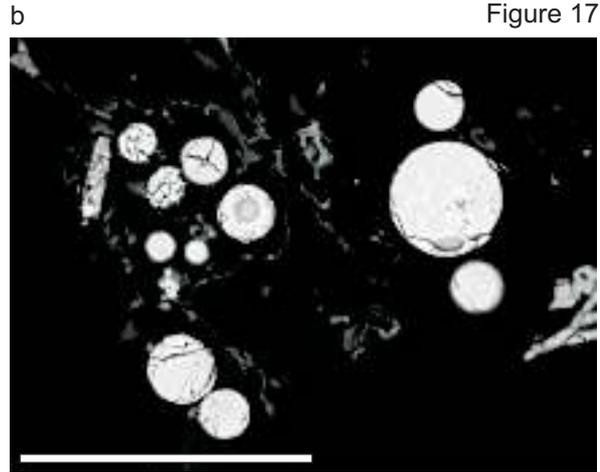
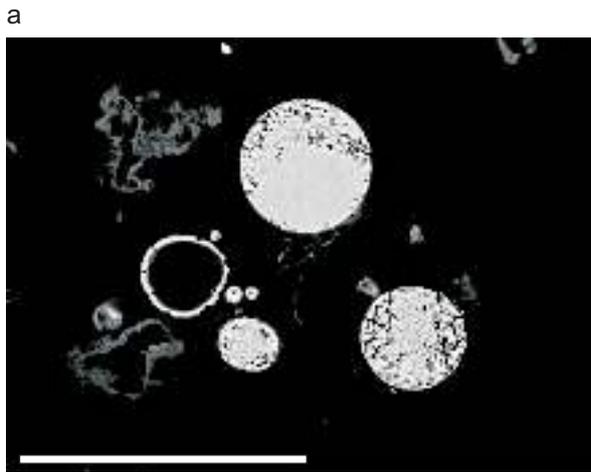


Figure 16



field of view 2mm



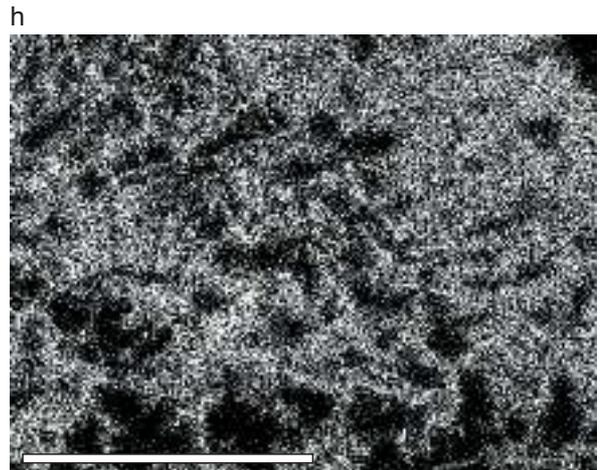
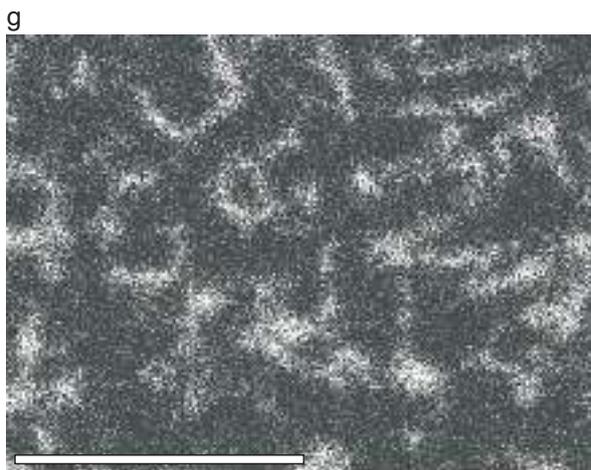
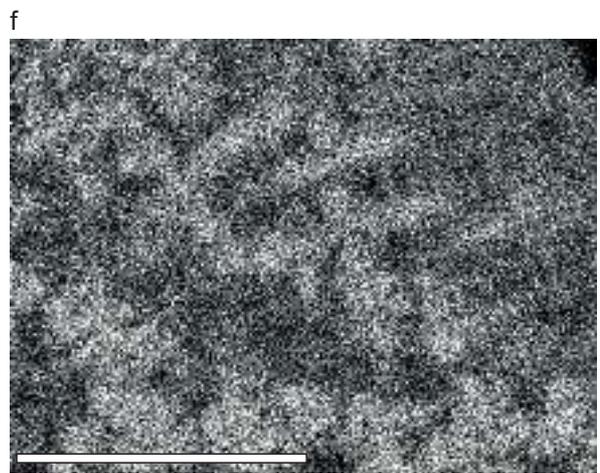
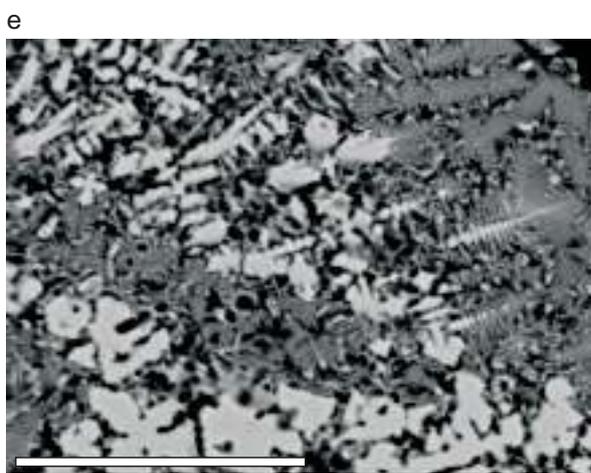
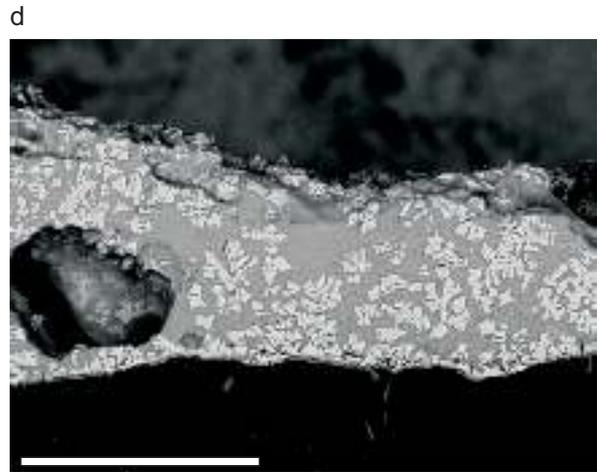
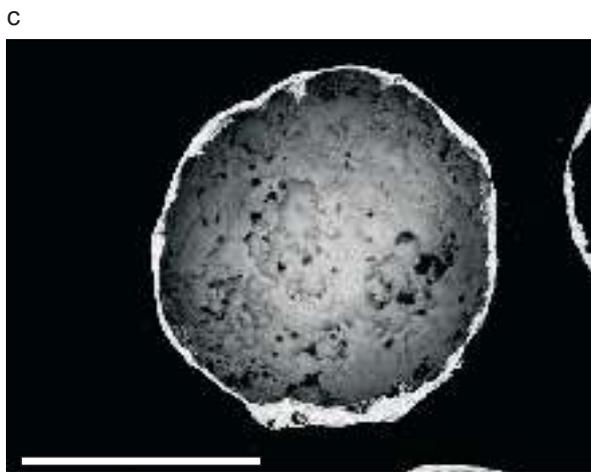
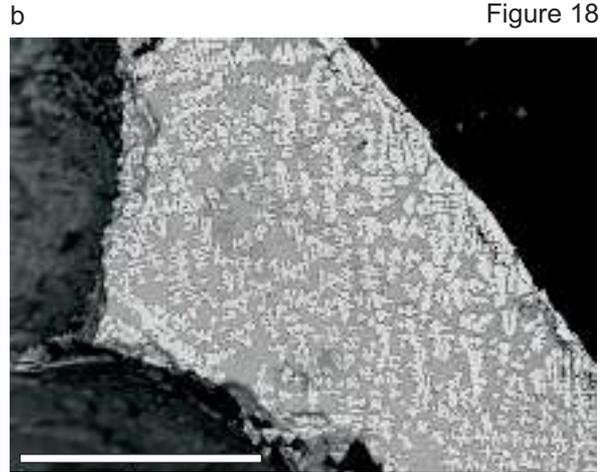


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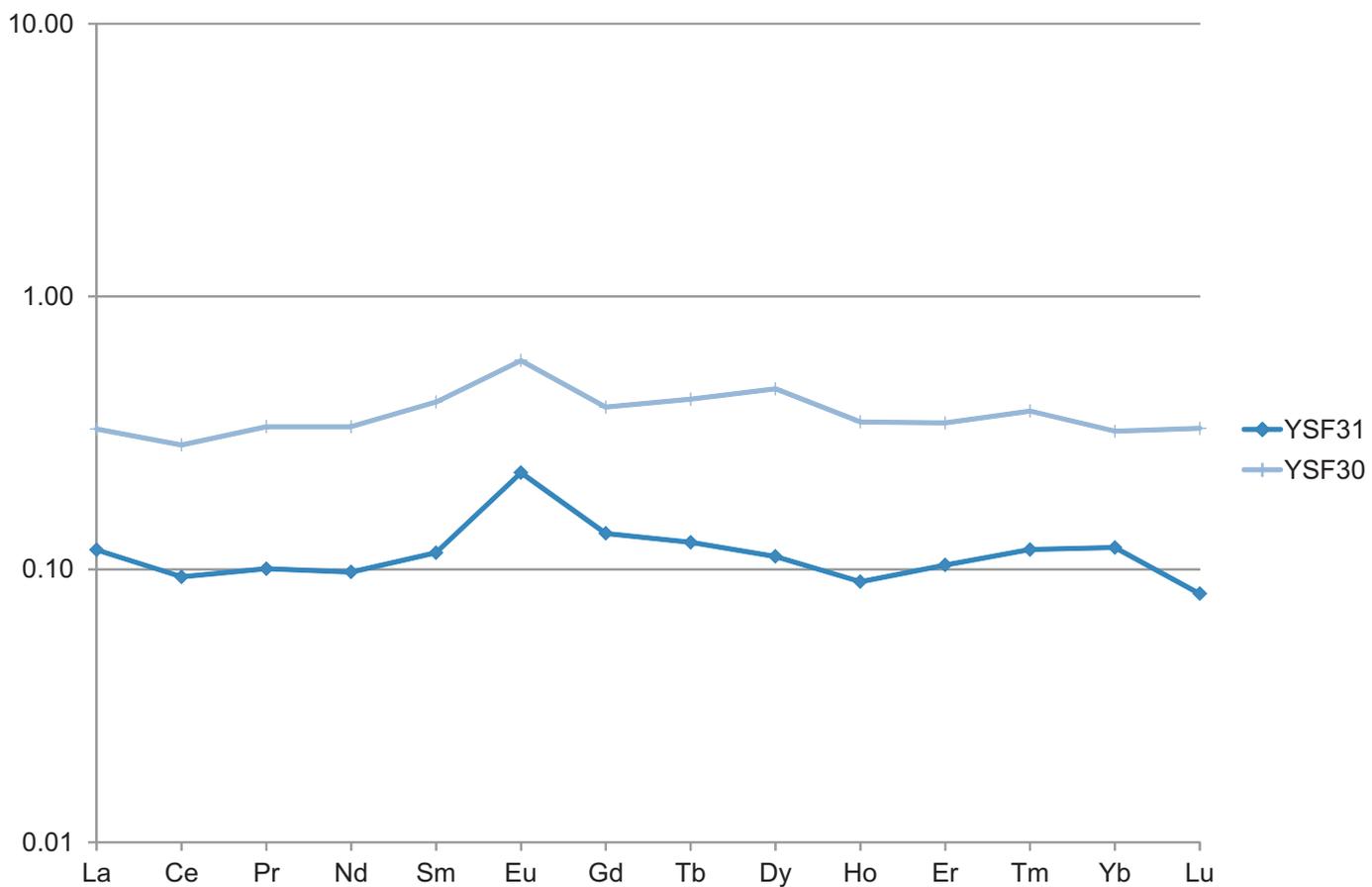
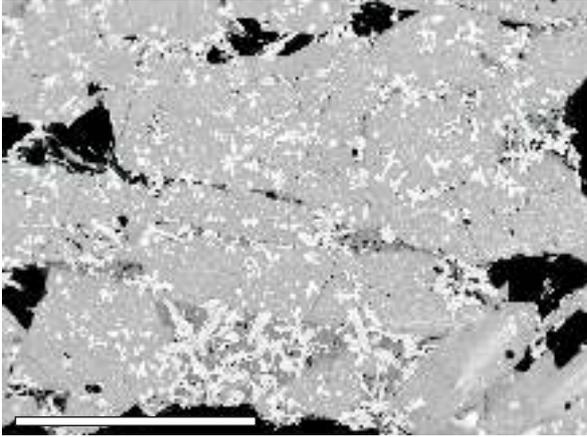
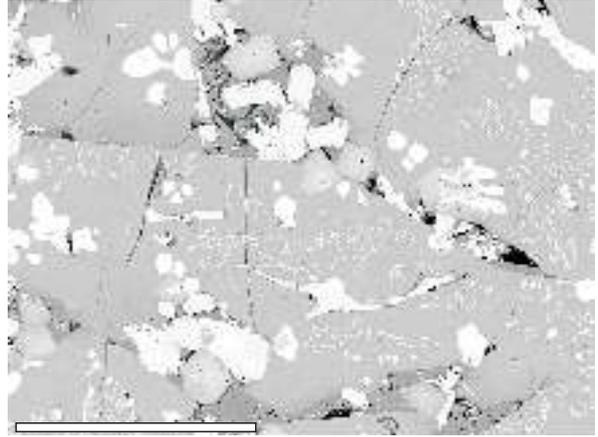


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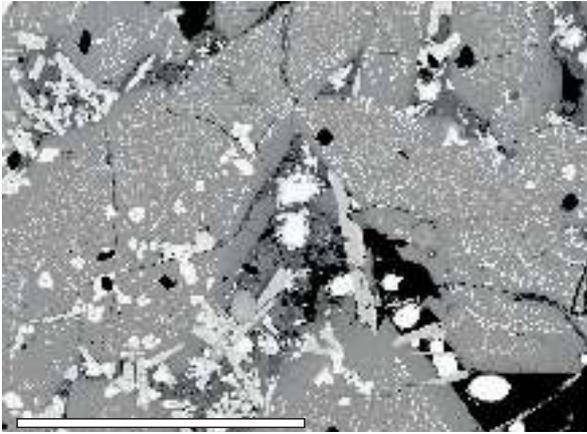
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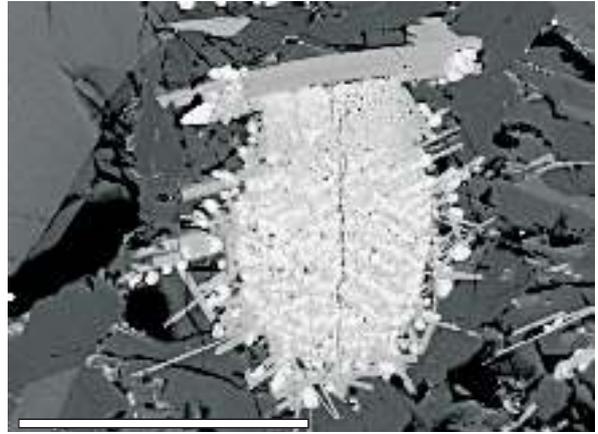
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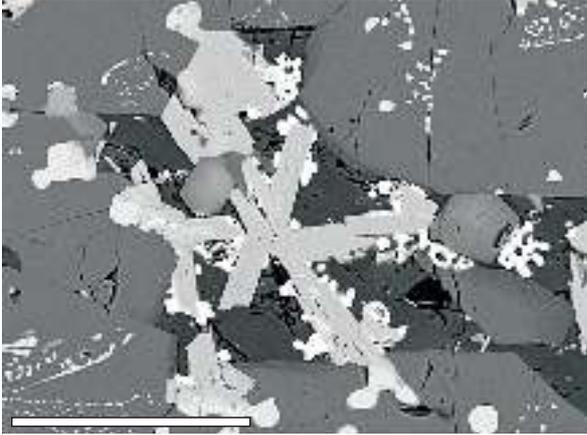
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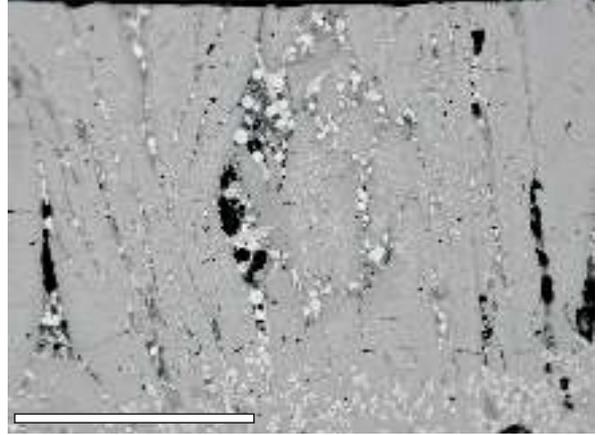
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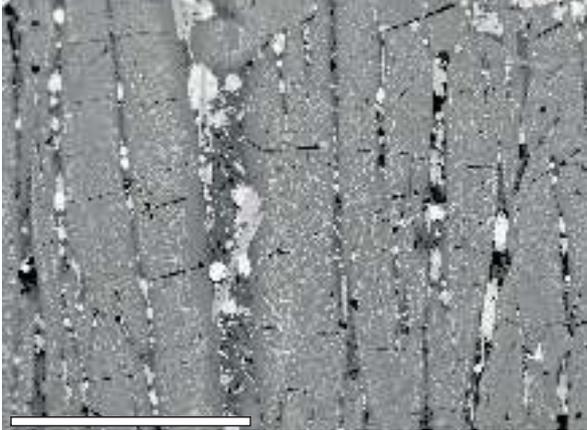
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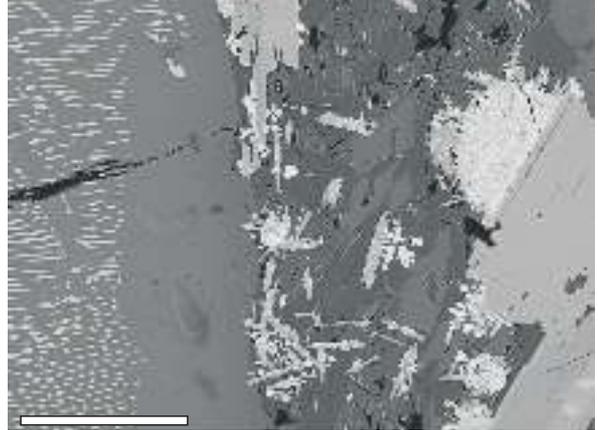


Figure 21



100mm

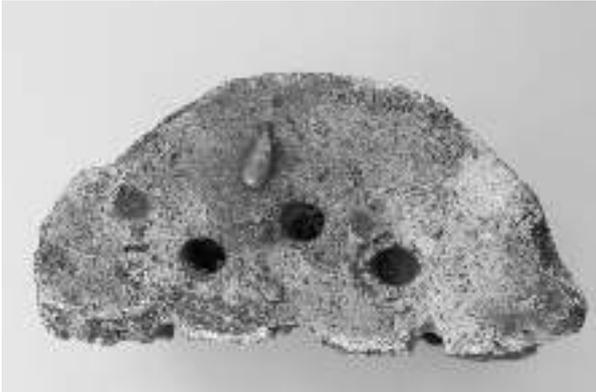


Figure 22

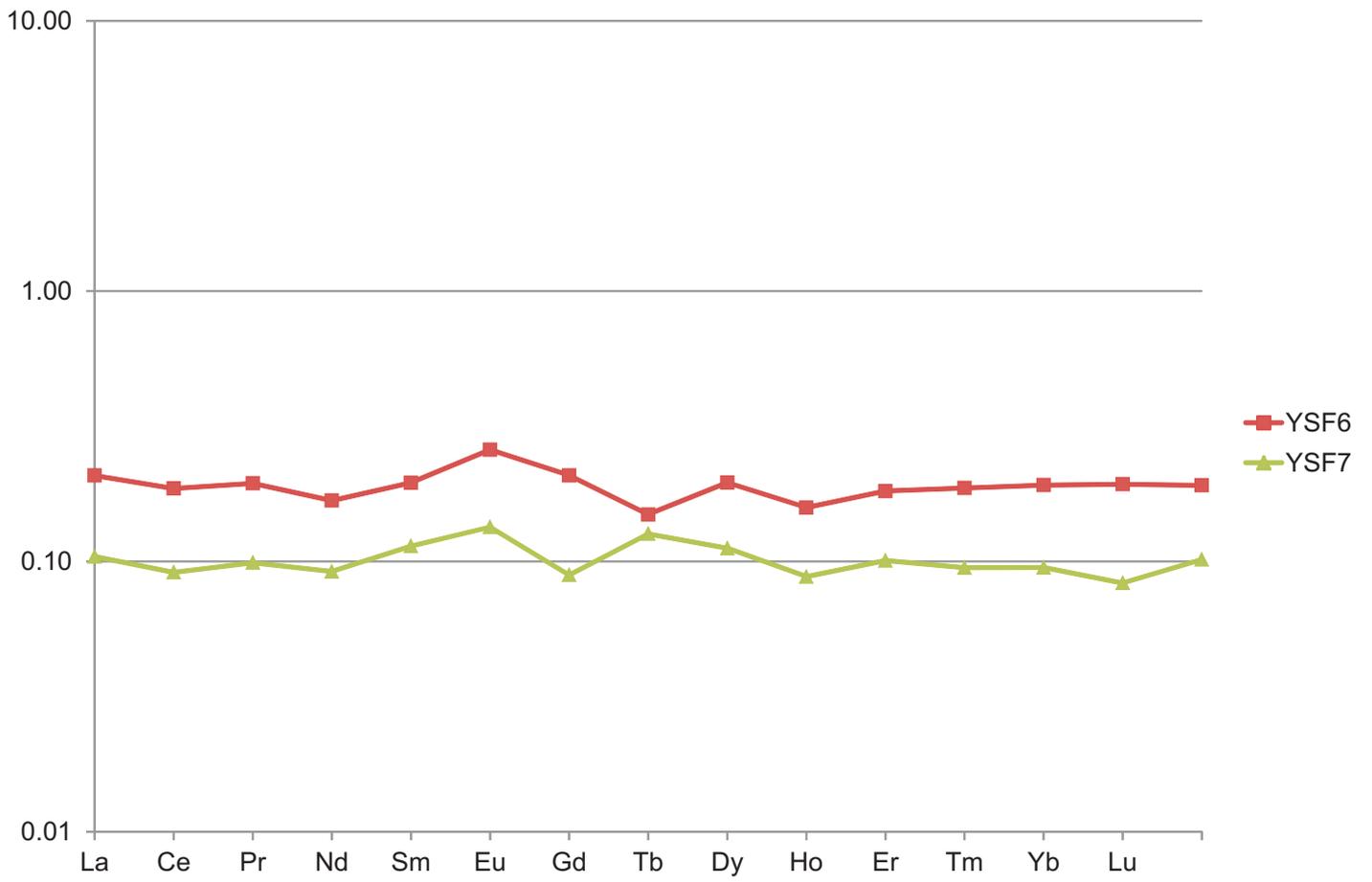


Figure 23

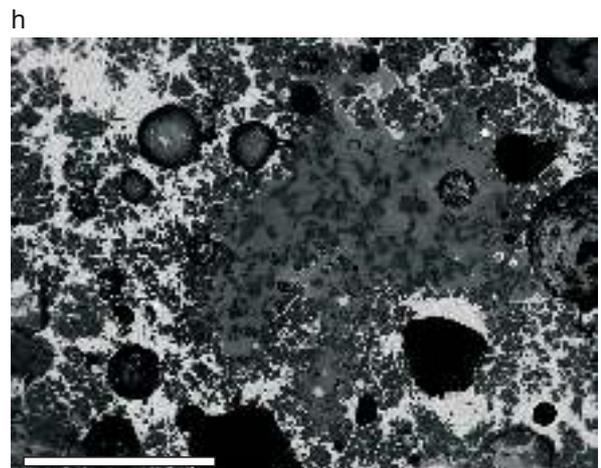
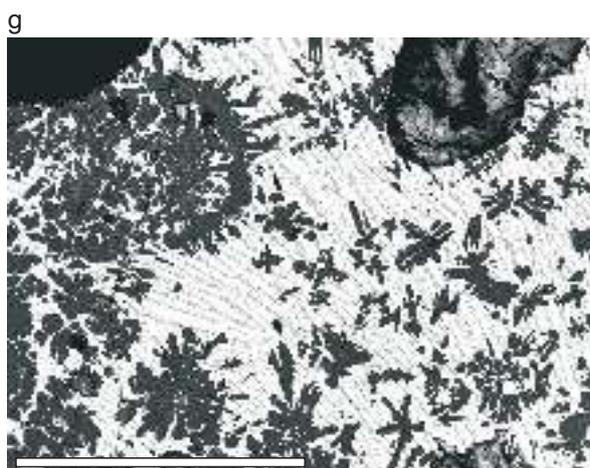
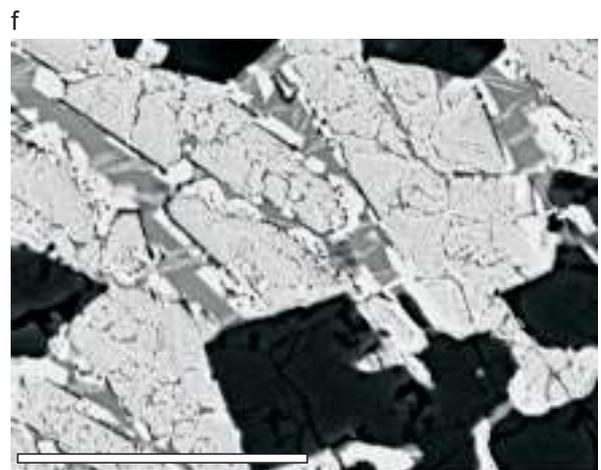
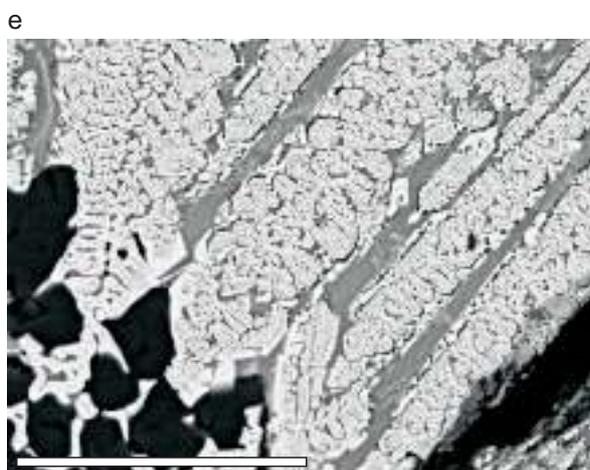
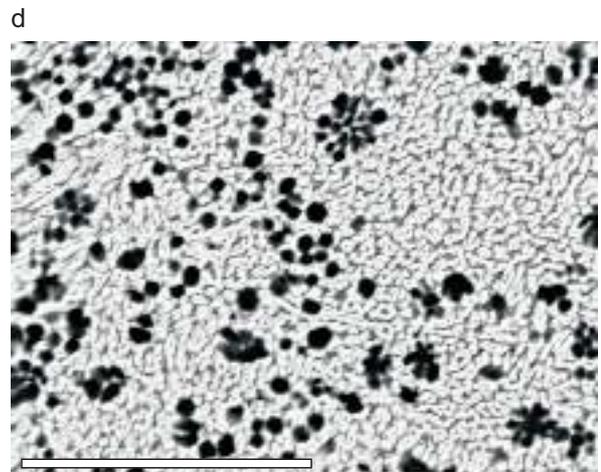
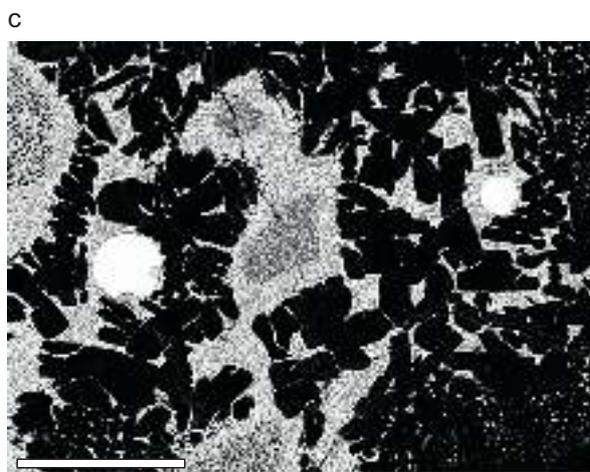
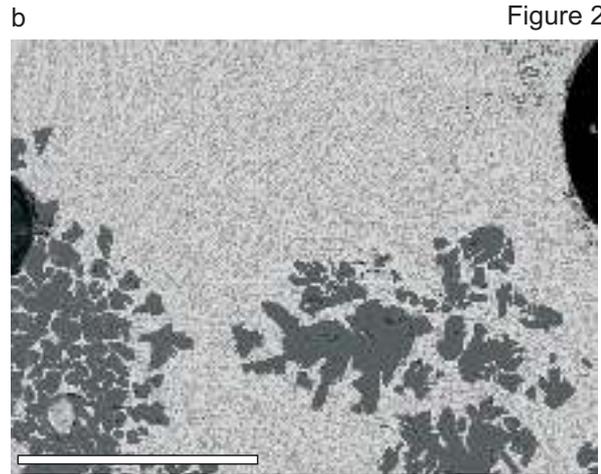
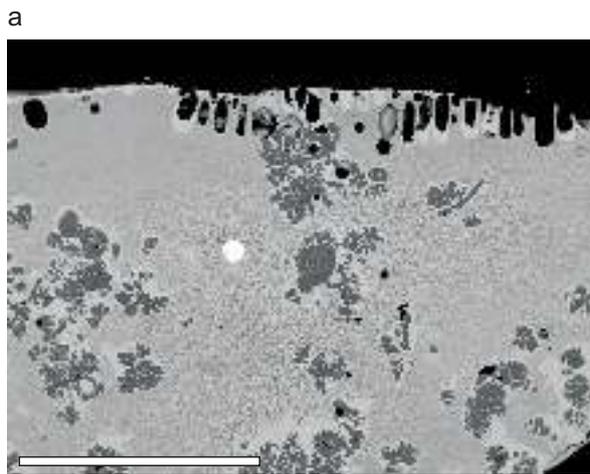


Figure 24

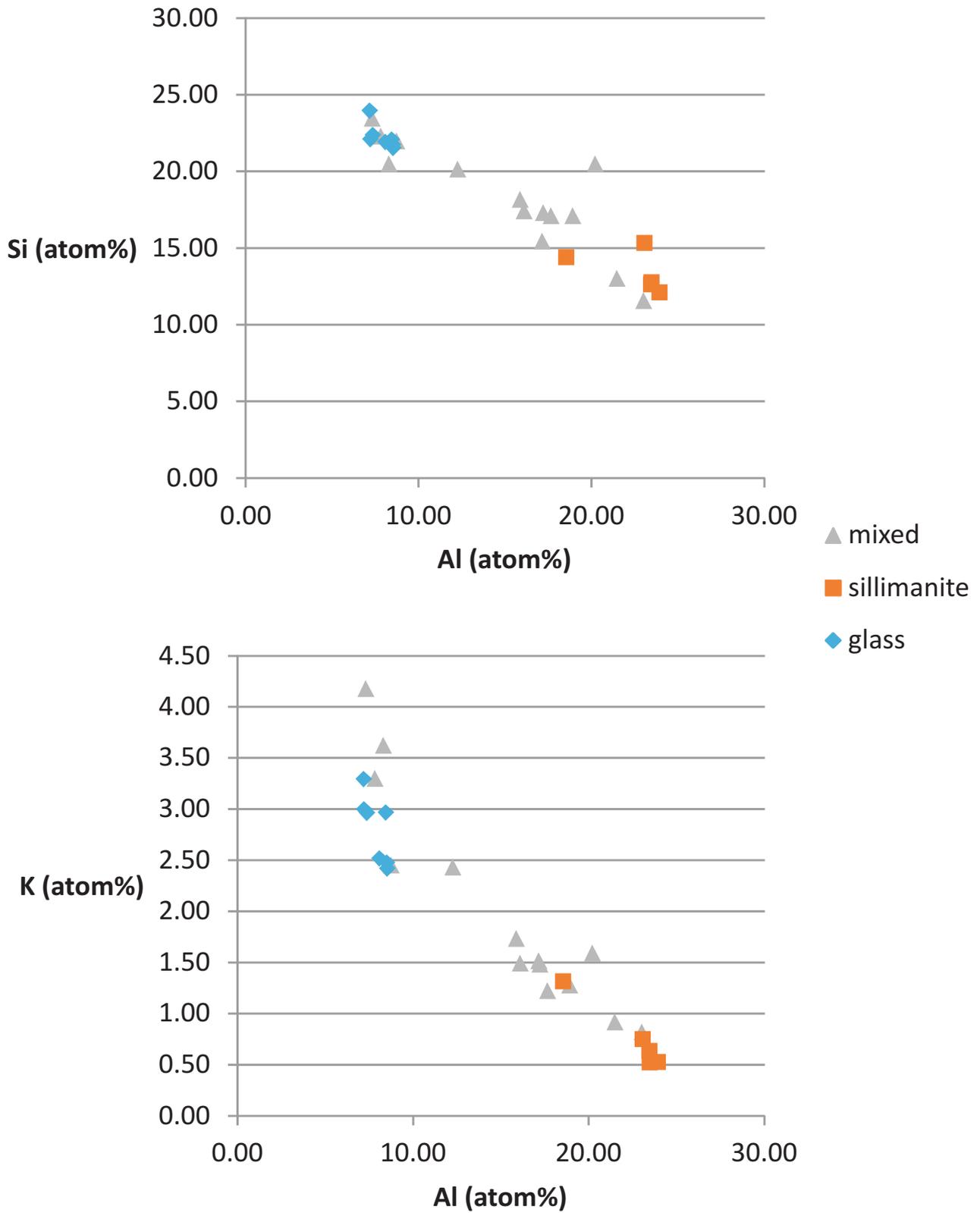


Figure 25

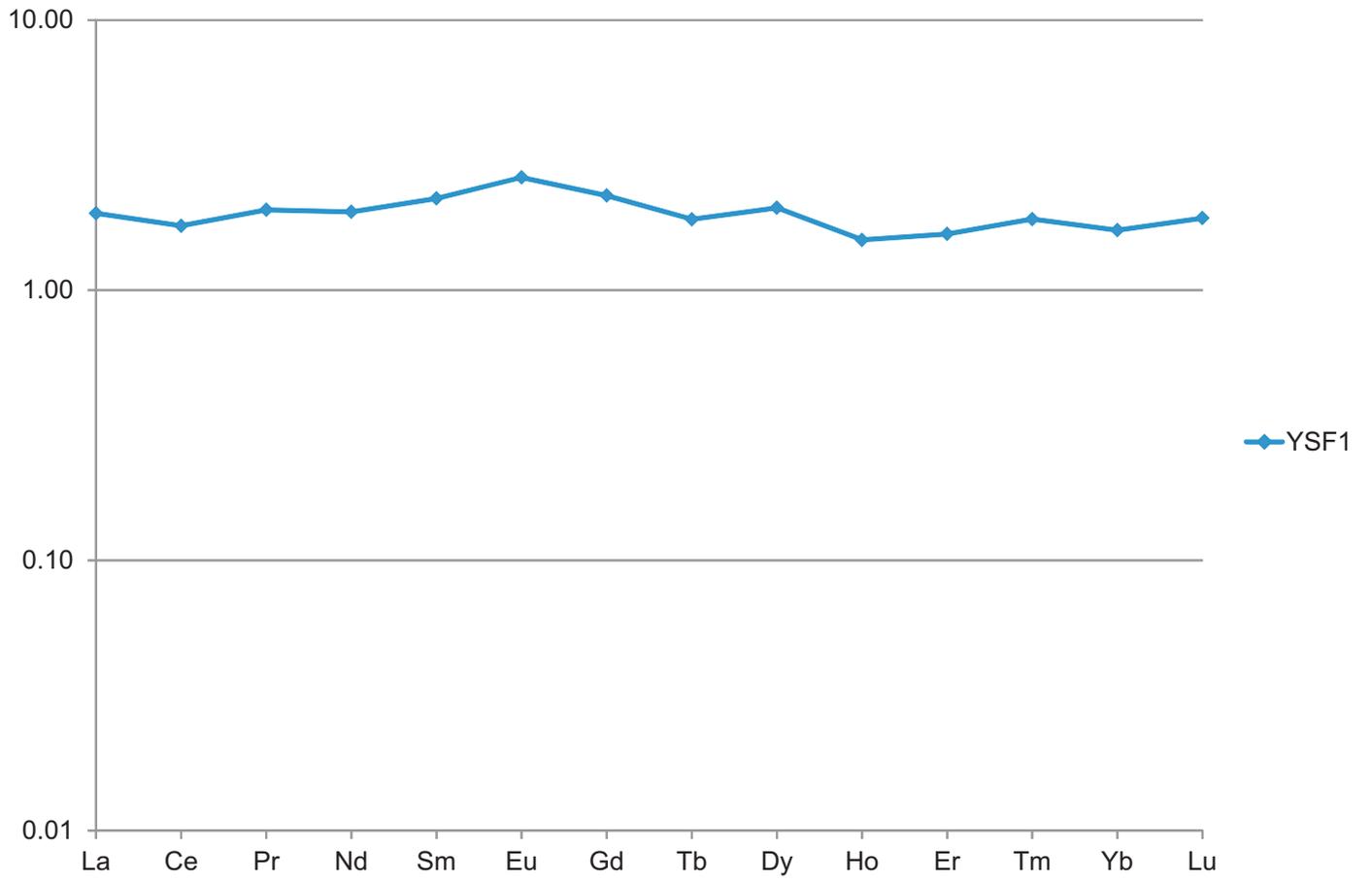


Figure 26

