Ancient Monuments Laboratory
Report 40/95

THE EXAMINATION OF IRON ARTEFACTS, RAW MATERIALS AND WASTE PRODUCTS FROM ROCKLEY BLAST FURNACE, WORSBOROUGH, SOUTH YORKSHIRE, 1978-82

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Summary

A range of materials and artefacts from the excavation of a historical blast furnace, believed to have been adapted to use coke rather than charcoal, were examined. Techniques included metallography, X-ray fluorescence (XRF) analysis and scanning electron microscope (SEM) based energy dispersive X-ray analysis (EDXA). Analysis confirmed the use of coke for smelting iron on the site and suggested that bloomery slag was used as a supplementary source of iron.

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Introduction

This report details the examination and analysis of a range of objects and materials recovered from the excavations directed by David Crossley at Rockley Blast Furnace (SE/338021) between 1978 and 1982. The major aim of the investigation was to distinguish the remains of documented early eighteenth century, charcoal fired, working (prior to a 1742 lease expiry) from possible later re-use of the site, which may have used coke as the fuel. Late eighteenth century activity had been suggested by secondary references, although the original documentation is believed to have been destroyed.

Macro Examination

The four iron objects were examined visually and by X-radiography before sampling. The location of samples was noted on drawings of the artefacts.

Metallographic Examination

Samples were cut from the objects and set in conductive Bakelite. The exposed section was prepared using standard metallographic techniques; grinding on successively finer abrasive papers then polishing with diamond impregnated cloths. The specimen was examined on a metallurgical microscope in both the "as polished" i.e., unetched condition and after etching in 2% nital (nitric acid in alcohol). A Shimadzu microhardness tester with 0.1kg load was used to determine the hardness of different phases within the metallographic structure.

Table 1. Material as supplied to AM Lab.

sample	context	context details/excavators comments
Charcoal	5	From working levels. Presumed to be from early eighteenth century operation
Charcoal	43	
Coke	113	Scatter from charging-ramp into head-race
Coke	86	A late context at the edge of the casting area , probably a wagon-loading/unloading point
Ore	31	As expected from the pits in the coal measures outcrops. From a working level.
Ore	113	Assumed from its weight to be ore, but differs in appearance from C5:31. Possibly roasted. From scatter on charging-ramp into the head-race silts, a context comparable with coke and limestone samples. Perhaps late 18th century
Limestone	113	Scatter from charging-ramp into head-race
Slag	32	Lowest filling of the furnace back-drain, a feature which appears to relate to a major rebuilding of the casting floor. This may be 'early' material used to form a porous drain-fill
Slag	15	Filling of the casting-pit, post abandonment levelling with accessible, presumably late, slag
Slag	76	Light-weight cindery material in head-race culvert. ? coking or ore roasting
Casting-sand/ metal or slag	61	Used as a fill for a hollow between the furnace and the charging-ramp abutment
Chisel	83	
Weigh beam part	5	
Pig	7	Cut from a pig found in the wheel-pit fill, with rubble: hence after abandonment of pit
Ladle	83	

X-ray Fluorescence (XRF) analysis

Unmounted pieces of the submitted samples were examined by semi-quantitative x-ray fluorescence (XRF) analysis. This allowed confirmation of the nature of the materials submitted for analysis, (for elements above fluorine in the periodic table), before more detailed microanalysis was undertaken.

Analyses were quoted only as 'strong', 'weak' and 'detected' on the basis of peak height. As no standards were compared it was not possible to be more precise on composition because peak height is dependent on a number of factors other than the true bulk composition of the material.

Scanning Electron Microscope (SEM) Energy Dispersive X-Ray (EDX) Microanalysis

The advantages of SEM based EDX analysis lie in the ability of the technique to undertake analysis at high magnifications on selected areas such as specific phases or mixtures of phases. The method is therefore highly suitable for heterogeneous archaeological materials. The sample may be viewed in back-scattered mode prior to analysis. This mode enhances atomic number contrast, rather than topography, allowing phases in the flat, polished specimen to be differentiated. Phases containing a large proportion of elements with higher atomic numbers appear lighter than low atomic number phases, such as glasses.

Analysis of designated areas of the sample were then undertaken using an EDX detector. A summary of the mean bulk SEM analyses is given in Table 2. Details of the area analyses of phases within the slag structures, and the replicate area analyses used to determine the bulk mean figures are listed in Appendix 1. Like XRF analysis, the technique detects elements rather than specific mineral forms. Although the "thin window" germanium detector used does allow the detection of lighter elements, including carbon, nitrogen and oxygen, determination of these elements can be problematic. Most samples were coated with carbon to prevent charging, and therefore the concentration of this element in these samples was not determined. However, some samples were analysed uncoated and approximate carbon contents are given. Figures quoted refer to the weight percentage of either elements or oxides. The oxides are derived from assumptions about the stoichiometry (*ie* the combining tendency) of each element. Assumed oxides were: Na_2O, MgO, Al_2O_3, $Si0_2$, P_2O_5, SO, K_2O, CaO, TiO_2, Cr_2O_3, MnO, FeO & NiO. The iron matrices of the metal samples together with phases which appeared to be sulphides, nitrides or carbonates are quoted as elemental weight percentages.

Table 2 Summary of analyses

SAMPLE	AREA	MODE	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni
charcoal(C5)		elem%	48.3	ns	43.5	0.2	0.8	0.1	0.2	nd	0.2	nd	0.1	6.1	nd	nd	nd	nd	ns
charcoal (C43)		elem%	49.3	ns	42.6	0.3	0.5	0.2	0.3	nd	0.5*	nd	nd	5.8	nd	nd	nd	nd	ns
coke (C113)		elem%	76.3	ns	16.4	nd	nd	0.8	0.9	nd	1.6	nd	0.2	0.9	nd	nd	nd	2.5	ns
coke(C86)		elem%	64.7	ns	24.3	nd	nd	1.1	1.3	nd	1.6	nd	nd	2.2	nd	nd	nd	3.9	ns
ore (C113)		elem%	6.2	ns	42.8	nd	1.5	5.0	11.3	nd	nd	nd	1.0	2.3	0.2	ns	0.4	28.8	ns
ore (C31)		elem%	9.0	ns	35.7	nd	nd	3.0	7.5	nd	nd	nd	0.7	0.6	0.2	ns	nd	41.7	ns
limestone (C113)		elem%	10.6	ns	51.6	nd	0.3	0.4	1.1	nd	nd	nd	nd	35.5	nd	ns	nd	0.2	ns
slag(C15)		oxide%	ns	ns	ns	nd	6.9	18.2	42.1	nd	nd	ns	3.4	18.6	0.9	nd	3.8	5.3	nd
slag (C32)		oxide%	ns	ns	ns	nd	6.8	18.1	42.3	nd	nd	ns	3.2	18.4	0.9	nd	3.8	5.8	nd
slag (C76)		oxide%	ns	ns	ns	nd	2.8	20.9	49.6	nd	nd	ns	3.4	0.9	1.2	nd	0.5	19.6	nd
casting	bulk	oxide%	ns	ns	ns	nd	2.2	8.1	72.4	nd	nd	nd	2.1	8.0	0.5	nd	1.1	4.3	nd
sand/slag	inclusion	oxide%	ns	ns	ns	nd	nd	0.1	96.9	nd	nd	nd	nd	nd	nd	nd	nd	1.7	nd
(C 61)	matrix	oxide%	ns	ns	ns	nd	4.7	13.7	57.9	nd	nd	nd	2.2	15.4	0.6	nd	2.3	2.5	nd
Chisel	iron	elem%	ns	ns	ns	nd	nd	0.05	0.08	nd	nd	0.04	nd	nd	nd	nd	nd	99.8	nd
(C 83)	inclusion	oxide%	ns	ns	ns	nd	nd	3.2	18.1	2.3	nd	ns	1.5	4.3	nd	nd	1.9	68.7	nd
	inclusion	oxide%	ns	ns	ns	nd	1.4	3.0	33.0	nd	nd	ns	1.7	8.4	nd	nd	30.4	22.2	nd
	inclusion	oxide%	ns	ns	ns	nd	2.3	3.8	44.1	nd	1.2	ns	1.8	9.2	nd	nd	28.0	9.5	nd
	inclusion	oxide%	ns	ns	ns	0.7	0.9	2.5	18.1	4.2	nd	ns	1.2	3.8	nd	nd	2.8	65.9	nd
	inclusion	oxide%	ns	ns	ns	1.1	1.7	5.5	44.6	nd	nd	ns	2.8	9.0	nd	nd	3.7	31.7	nd
	inclusion	oxide%	ns	ns	ns	0.6	1.5	3.9	38.9	nd	0.7	ns	2.0	8.6	nd	nd	28.1	15.8	nd
	inclusion	oxide%	ns	ns	ns	nd	2.0	3.3	45.8	nd	1.1	ns	1.6	10.4	nd	nd	30.2	5.6	nd
	inclusion	oxide%	ns	ns	ns	0.6	0.3	3.1	59.7	nd	nd	ns	1.7	3.6	nd	nd	3.4	27.7	nd
	inclusion	oxide%	ns	ns	ns	1.2	0.6	4.3	21.5	7.0	nd	ns	2.5	5.6	nd	nd	2.6	54.8	nd
	inclusion	oxide%	ns	ns	ns	1.5	0.5	2.8	28.3	3.0	0.4	ns	1.3	4.2	nd	nd	2.1	55.8	nd
	inclusion	oxide%	ns	ns	ns	0.4	2.0	2.7	37.6	0.3	0.4	ns	1.2	8.4	nd	nd	28.3	18.7	nd

SAMPLE	AREA	MODE	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni
weigh	steel	elem%	ns	ns	ns	nd	nd	0.1	0.3	nd	nd	nd	nd	nd	nd	nd	0.4	99.2	nd
beam	iron	elem%	ns	ns	ns	nd	nd	0.1	0.1	nd	nd	0.1	nd	nd	nd	nd	nd	99.8	nd
part	inc(iron)	oxide%	ns	ns	ns	nd	nd	nd	7.2	1.9	nd	ns	nd	nd	nd	nd	1.5	89.4	nd
(C5)	inc(iron)	oxide%	ns	ns	ns	nd	nd	nd	11.0	7.7	1.6	ns	nd	nd	0.4	nd	1.1	78.3	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	2.1	16.7	4.3	0.8	ns	nd	0.4	0.6	nd	2.8	72.3	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	1.5	8.4	3.8	nd	ns	nd	0.4	nd	nd	1.4	84.6	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	0.9	11.3	7.9	nd	ns	nd	0.5	nd	nd	1.3	78.1	nd
	inc(steel)	oxide%	ns	ns	ns	nd	nd	2.5	73.1	nd	0.3	ns	nd	nd	0.3	nd	6.0	17.8	nd
	inc(steel)	oxide%	ns	ns	ns	nd	nd	2.4	76.3	nd	nd	ns	nd	nd	nd	nd	4.7	16.6	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	nd	17.4	9.0	nd	ns	nd	0.5	nd	nd	2.1	71.1	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	nd	3.0	2.3	nd	ns	nd	0.2	nd	nd	0.9	93.6	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	2.3	18.3	5.1	0.8	ns	nd	0.3	0.4	nd	4.9	68.0	nd
	inc(iron)	oxide%	ns	ns	ns	nd	nd	nd	11.7	10.5	1.2	ns	nd	0.4	0.1	nd	1.7	74.4	nd
	weld inc.	oxide%	ns	ns	ns	nd	nd	nd	1.3	nd	nd	ns	nd	nd	nd	nd	0.7	98.0	nd
Pig	iron	elem%	ns	ns	ns	nd	nd	0.07	0.36	0.88	0.17	0.06	nd	nd	nd	nd	0.6	97.8	nd
elem%	inclusion	elem%	ns	nd	nd	nd	nd	nd	nd	nd	35.7	nd	nd	nd	nd	ns	64.3	nd	nd
	inclusion	elem%	ns	nd	nd	nd	nd	nd	nd	nd	35.8	nd	nd	nd	nd	ns	64.2	nd	nd
	inclusion	elem%	ns	17.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	78.5	ns	nd	4.5	nd
	inclusion	elem%	ns	17.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	77.8	ns	nd	4.5	nd
	inclusion	elem%	ns	nd	nd	nd	nd	nd	nd	1.6	29.0	nd	nd	nd	nd	ns	57.3	12.1	nd
Ladle	iron	elem%	ns	ns	ns	nd	nd	nd	0.48	nd	nd	nd	nd	nd	nd	19.2	1.6	78.7	10.4
(C83)	inclusion	oxide%	ns	ns	ns	nd	nd	34.4	38.9	nd	3.4	ns	nd	nd	1.3	5.8	nd	16.2	nd
	inclusion	oxide%	ns	ns	ns	4.2	2.8	8.5	26.6	1.4	9.5	ns	1.8	17.7	1.2	5.2	0.4	20.7	nd
	inclusion	oxide%	ns	ns	ns	nd	nd	7.8	35.2	nd	nd	ns	nd	nd	nd	18.1	37.9	1.0	nd
	inclusion	oxide%	ns	ns	ns	nd	nd	nd	36.3	nd	0.8	ns	nd	nd	nd	17.0	45.9	nd	nd

ns = not sought nd = not detected * skewed by single high value

Results of the examination:
The Raw Materials

Charcoal from Context 5 (sample930005/11)
The slag from the floor of the bellows house included fragments from either Salix sp. (willow) or Populus sp. (poplar) each showing approximately 16 years growth. The SEM EDX analyser had difficulty in differentiating carbon from oxygen. The sulphur content of 0.1 to 0.4%, is much lower than that for coke. The charcoal did however contain greater amounts of calcium and magnesium

Charcoal from Context 43 (sample930005/14)
Charcoal from the East working area contained fragment from a single branch or stem of Fraxinus sp. (ash) showing about 15 years growth. Analysis was similar to sample 930005/11 but one spot analysis gave a much higher sulphur content (1.2%), probably due to sample contamination.

Coke from Context 113 (sample930005/13) &Coke from Context 86 (sample930005/10)
XRF analysis of both samples was sufficiently sensitive to identify the presence of sulphur. This was quantified on the SEM EDX analyser, which indicated a content of 1.3 to 2.1% with both samples averaging 1.6%. The two samples are sufficiently similar to suggest the same source.

Ore from Context 113 (sample930005/5)
Individual mineral grains within the ore corresponded to the composition of siderite ($FeCO_3$). 5 analyses of the surface gave a mean iron content of 28.8% and silicon content of 11.3%. A viable, though not particularly rich ore.

Ore from Context 31 (sample930005/6)
Like the previous sample grains of siderite ($FeCO_3$) were found within the ore. 5 analyses of the surface gave a mean iron content of 41.7% and silicon content of 7.5%. Clearly a much richer ore than 930005/5.

Limestone from Context 113 (sample930005/9)
Almost pure calcium carbonate ($CaCO_3$) with some silicon and traces of magnesium, aluminium and iron.

The Waste Products

Slag from Context 32 (sample930005/4)
This was of a glassy morphology typical of blast furnace slag. The colouration was almost black but slightly translucent with approximately 5% porosity. Analysis showed high levels of calcium and aluminium which, in blast furnace slags, combine with silica from the gangue to form a glassy slag. No sulphur was detected in the sample and the slag is therefore unlikely to derive from coke smelting. Iron oxide (FeO) levels are correspondingly low, averaging 5% and indicating a reasonably efficient extraction of iron.

Slag from Context 5 (sample930005/1&2)
Although slightly less porous than the slag from Context 32, the compositions of these two slags are essentially the same in all elements and this is also a typical charcoal-fuelled blast furnace product.

Slag from Context 76 (sample930005/3 & 12)
The very porous, crumbly nature of this slag initially suggested that it might have been produced during a coking process. Many oxides (aluminium, potassium, titanium and silicon) showed similar levels to the two "typical" blast furnace slags. However, the iron oxide content is much higher (19.6%), calcium is virtually absent and magnesium is present in much lower concentrations. The low manganese oxide content would tend to imply the slag results from neither a smelting nor a fining operation, and the absence of sulphur argues against coking. Its technological origins are therefore uncertain.

Casting-sand/metal or slag from Context 61 (sample930005/7)
This sample comprised a mass of sand which had been concreted together with iron hydroxides and had a slaggy, vitrified surface on one side. Microscopic examination of this slagged material revealed a matrix of glassy material surrounding partly reacted quartz grains. Microanalysis showed the grains to be silica with traces of iron and aluminium. The matrix was rich in silica (57.9%) but also contained oxides of calcium (15%), aluminium (14%) and all the other elements found in the blast furnace slag samples, although at slightly lower levels. The crust appears to have been formed by the reaction between the casting floor sand and liquid slag, rather than hot metal.

The Four Iron Objects (Plate1 & Figure 1)

The Chisel (Context 83)
The chisel was submitted for examination to determine its manufacturing technology, in particular whether a steeled cutting tip had been incorporated into the artefact. Although superficially pitted, the corrosion on the chisel had not severely penetrated the structure. X-radiographs were made at different power settings, through both front and side elevation of the artefact to locate any welds associated with steeling of the cutting tip. However, no evidence for this was found. A small V-notch was then cut in the tip for metallographic examination. In the unetched condition about 2 % of dual and single phase slag stringers were evident elongated along the length of the shaft. Etching in nital revealed a poorly etched band running through the centre of the sample. Three structures were identified, each resulting from slightly different heating and cooling conditions during the heat treatment of the object: The tip comprised tempered martensite with a grain size of ASTM 5 and a micro-hardness of H_v 562. The opposite, thicker, end of the sample comprised a widmanstätten structure with up to 5% grain boundary ferrite surrounding bainite (H_v 220). Along one edge of the sample three small areas of retained austenite (H_v 872) within plate martensite (H_v 395) were found.

Analysis of the matrix revealed no significant level of any impurity element. Carbon was not determined, but given its martensitic structure the material can certainly be classified as a steel. Several distinct types of inclusion were identified. Some of largely fayalitic composition were unusual only in the relatively high phosphorus concentrations (up to 8% oxide). Others contained remarkably high levels of MnO (to 30%) as well as calcium oxide (to 10%). A single high FeO inclusion probably

resulted from entrapped scale.

The very high level of manganese and phosphorus in the inclusions, but not in the metal matrix, suggest that the metal has at some stage passed through either a finery or puddling hearth which has oxidised these elements from the metal. It is not possible to determine whether the high carbon content was achieved directly from this process or by subsequent carburisation. The tip of this tool was heat treated to give a very hard, but tough, cutting edge.

Weigh beam part (Context 5)

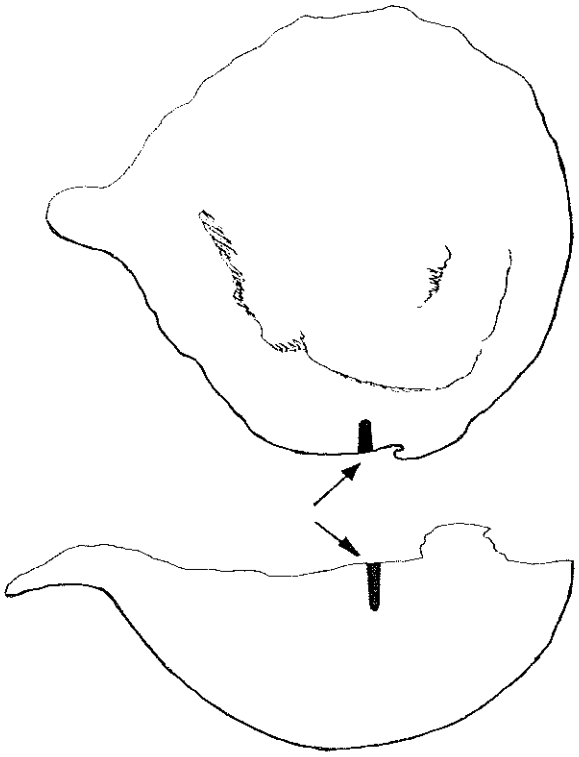
This was a "T" shaped artefact with a round shaft protruding 110mm from the underside of a 155mm long bar of triangular section. The purpose of the object was unknown, although a possible explanation was that it formed the pivot for a weigh beam. Strategraphically the object derived from an early context (C5, the bellows house occupation level). Examination was undertaken to determine the material and means of construction, with the aim of understanding its function.

Visual examination showed it to have corroded to a similar extent to the chisel. The round shaft showed traces of a screw thread and the triangular-sectioned head showed two recessed grooves along one face. X-radiography showed no traces of any weld lines, at this or any other position, which might have been associated with the butt welding of a steel edge to the apex of the triangular section. However, the X-radiograph did show a wide but shallow void between the end of the shaft and the hole into which it was fitted and the joining of these two parts would appear to be by welding.

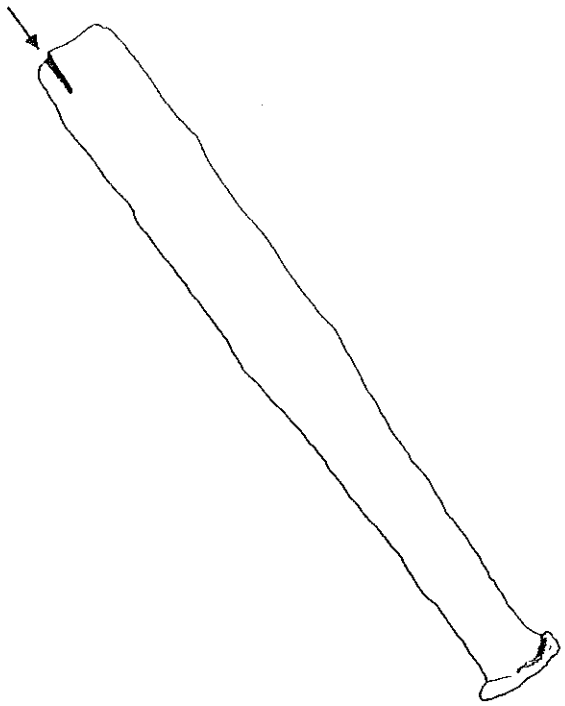
A small wedge cut from the apex of the triangular section, showed that the artefact was of composite construction, but used a "sandwich" rather than butt welding technique to achieve this. In the unetched condition the central material was seen to be almost free of slag (1% single phase spheroidal inclusions), whilst the outer material contained approximately 5% of multiple-phased inclusions. Etching in nital preferentially etched the central region and a broad, darkened, cental band could be seen. Under the optical microscope the steel was found to comprise 80% of fine pearlite (ASTM 6, H_v214), 20% ferrite, indicating an air cooled steel of approximately 0.6% carbon. The sides of the section comprised carbon free ferrite (ASTM 5-6, H_v135), except for a narrow band where some carbon diffusion, from the steel to the iron, had occurred.

Microanalysis of the metal phases showed the iron to be almost free of trace elements, whilst the steel contained 0.4 % manganese and 0.3% silicon. Inclusions in the steel were largely composed of silica, and possibly derived from sand used as a welding flux; it was impossible to determine more about the origins of the metal. Inclusions in the iron were predominantly fayalitic (iron silicate) but contained significant quantities of oxides of phosphorus (2-10%) and manganese (1-6%). These probably originate from a finery (or puddling) hearth. Considerable effort had clearly been taken in providing the object with a steel edge, though it was surprising that no attempt had been made to harden this by heat treatment. Even so the additional hardness and toughness would have given some advantage over the use of low carbon iron if the object did function as is suggested-as the pivot of a weigh beam.

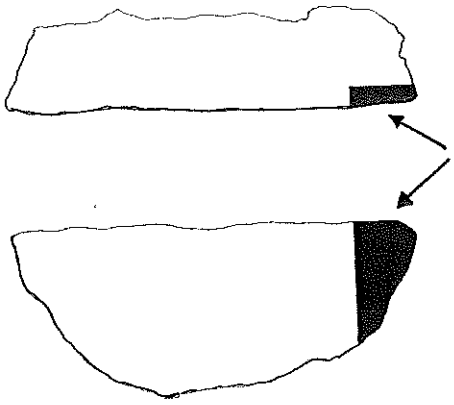
Plate 1 The iron artefacts from Rockley Blast Furnace



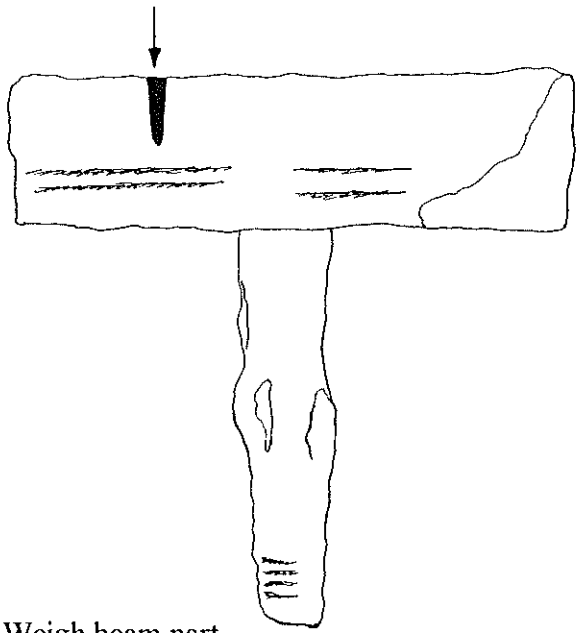
Ladle residue
(AML Sample No. 930001)



Chisel
(AML Sample No. 930002)

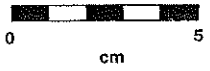


Cast iron pig
(AML Sample No. 930003)



Weigh beam part
(AML Sample No. 930004)

Figure 1 The iron artefacts showing sample position



The Cast Iron Pig (Context 7)
Stratigraphically, the pig belonged to a late context, assumed to be related to the later re-use of the furnace. It was therefore hoped that examination and analysis would determine the fuel used in its production. The end of the iron pig had already been detached from the complete ingot when submitted for analysis. The sample section was approximately semi-circular, being 45mm deep and 110mm wide.

Although heavily corroded on the exterior and having some oxide penetration through the voids left by the graphite flakes, approximately 90% of the volume of the metal remained unaffected. X-radiography revealed some low density regions where corrosion had penetrated the surface but revealed no other features of interest. The metallographic specimen, viewed before etching, revealed a network of graphite flakes within the iron matrix, suggesting a grey cast iron. Etching in nital showed a more complex structure: The graphite flakes were surrounded by coarse pearlite (H_v301), but large areas of cementite were also present (H_v983). In addition a further phase, probably iron phosphide eutectic, was visible in bands. A small quantity (<1%) of small "dove grey" polygonal inclusions were present.

Micro-analysis of the iron matrix revealed approximately 0.6% manganese, 0.9% phosphorus, 0.4 % silicon & 0.17% sulphur. The inclusions, except for a single iron oxide example were mostly manganese sulphide but titanium nitride inclusions were also present. The presence of significant quantities of sulphur, both in inclusions and in the matrix, indicates that this material was the product of high sulphur fuel, such as the coke found on the site.

The Ladle Residue (Context 83)
The object described as a "ladle and solidified contents" was found to be only the latter (a skull), although it retained the ladle shape, including the pouring spout. It's surface was of black, semi lustrous appearance, suggesting high temperature scaling rather than post-depositional corrosion. X-radiography revealed no features of interest.

It had been assumed that the residue was cast iron. However, during metallographic preparation its total resistance to the nital etchant raised some doubts as to its composition. X-ray fluorescence analysis revealed high concentrations of chromium and nickel. The sample was therefore subjected to a more appropriate etchant (50% hydrochloric acid, 25% nitric acid, 25% water) This revealed large austenite dendrites (H_v182) extending inwards from the surface together with approximately 5% of a grain boundary phase.

SEM/EDX analysis gave the composition of the alloy as 17.5% chromium, 9.0% nickel and 1.4% manganese. This is consistent with austenitic stainless steels, produced only from the second decade of the twentieth century. As the site of Rockley was certainly not active at this period, it is assumed that this artefact results from contamination of archaeological layers following the dumping of modern metallurgical debris on the site.

Mass balance

These calculations look at the total mass of the constituent elements in the chemical reactions within the smelting process. It makes use of known factors such as composition of the raw materials and products and can help to derive figures for unknowns such as the proportion of each component. The value of such a calculation is limited by a number of factors:

- Samples examined during this investigation may have originated from either charcoal or coke smelting phases.
- A complete range of raw materials, products and waste products do not exist for either mode of operation.
- Further chemical input from furnace lining and other possible sources should be expected.
- The quantities of each material in the balance is unknown.
- The analysis of the pig iron is of the iron matrix not bulk composition and will therefore underestimate manganese, sulphur and titanium content.

Despite these problems, there is some value in attempting such a calculation. In the balance below the composition of the higher grade ore from C5:31 is used whilst figures for glassy slags and coke are averaged.

A first calculation was based on 100kg ore, which if almost all its iron was converted to pig and all silica to slag, would produce 40kg of cast iron and 40 kg of glassy slag respectively. Coke consumption is estimated as 60kg and this would leave a shortfall in the calcium content, which would be made good by the addition of 5kg limestone. Subtracting the total weight of other elements in the products from those of the raw materials leaves several imbalances: An excess of potassium and aluminium in the products might be explained as the result of not including the contribution from the furnace lining. A lack of sulphur results from the comparison of high sulphur coke with a slag which derived from a charcoal smelt: hence, a slag containing in the region of 0.5 % sulphur would be expected for this process. More striking is the excess of phosphorus, manganese and magnesium; the first two of which fail to appear in detectable quantities in any of the raw materials.

	Total	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
ore (kg)	100	0	2.96	7.54	0	0	0.70	0.58	0.20	0	41.71
coke (kg)	60	0	0.34	0.40	0	0.58	0	0.55	0	0	1.17
limestone (kg)	5	0.01	0.02	0.06	0	0	0	1.77	0	0	0.01
iron (kg)	40	0	0.03	0.15	0.35	0.07	0	0	0	0.25	39.13
slag (kg)	40	1.64	3.84	7.93	0	0	1.10	3.11	0.21	0.25	1.73
balance (kg)		1.63	0.55	0.08	0.35	-0.51	0.40	0.20	0.01	0.50	-2.02

Although magnesium in charcoal could have contributed to the (charcoal) slag, it would not have contributed any manganese or phosphorus to the products. The most likely source of these elements would be the re-smelting of old bloomery slags. The site of Rockley blast furnace lies within a few hundred meters of an earlier bloomery furnace excavated in 1964 (Crossley 1967). Analyses, quoted by Morton and Wingrove (1972), from this site show that this material did contain significant concentrations of manganese, phosphorus and magnesium, indicating the use of a different ore source at that date (possibly a bog ore unsuitable for the higher stack of a blast furnace).

The calculation was repeated but with the one third of the weight of ore replaced with bloomery slag. This brought the levels of manganese and phosphorus roughly into line with the products of the furnace. The difference in level of magnesium is also narrowed. Other elements change only slightly. Although the addition of bloomery slag would certainly lessen the yield obtained from ore C5:31, it would make almost no difference to the leaner ore C18:2.

		Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
ore	67kg	0	1.98	5.03	0	0	0.47	0.58	0.14	0	27.82
bloomery slag	33kg	0.36	2.42	4.21	0.26	0	0	0.98	0	0.54	10.22
coke	60kg	0	0.34	0.40	0	0.58	0	0.55	0	0	1.17
limestone	5kg	0.01	0.02	0.06	0	0	0	1.77	0	0	0.01
iron	40kg	0	0.03	0.15	0.35	0.07	0	0	0	0.25	39.13
slag	40kg	1.64	3.84	7.93	0	0	1.10	3.11	0.21	0.25	1.73
balance		1.27	0.89	-1.62	0.09	-0.51	0.63	-0.58	0.08	-0.04	1.64

Conclusions

High levels of sulphur in the cast iron pig point to the use of sulphur rich coke, (such as the two samples examined in this project), as fuel to smelt iron on the site. The stratigraphy of these finds would indicate that this use of coke occurred during a late phase of activity on the site.

Charcoal from earlier contexts of the site suggests the use of coppice wood for the production of charcoal for fuel.

Two artefacts from the site; a chisel and an object interpreted as part of a weigh beam showed evidence of knowledgable heat treatment and skilled smithing ability in combining dissimilar ferrous alloys into a composite artefact. The technology for the production of the metal in these artefacts would appear to be the indirect process *i.e.* the blast furnace and finery or puddling hearth.

The analytical programme was able to examine and investigate the composition of a wide range of raw materials, products and waste products from the operation of the blast furnace at Rockley. Caution must be taken in assuming that all raw materials (except fuel) remained consistent through the long life-span of the furnace. Although there were insufficient samples to fully investigate this, duplicate samples of coke and glassy slag did show very similar compositions. A second sample of ore proved of a low grade, it may have been rejected for this reason. The existence of iron ore and coal deposits within one mile of the site. (David Crossley pers comm.) could also be used to argue against the likelihood of different materials being transported in to the site.

Mass balances showed that the materials examined in this study did not comprise the totality of the raw materials and products of the smelting process. The slag was found to contain insufficient sulphur to derive from the coke smelting phase. Additionally, the analysis of the ore indicated that it contained insufficient phosphorus and manganese to produce the cast iron pig (and a corresponding coke-smelting slag). It is proposed that this is due to the re-use of slag from the nearby bloomery furnace at Rockley Smithies.

Storage of Samples

All artefacts, negatives, x-radiographs, transparencies and prints with copies of recording sheets to be archived at Sheffield Museums. Mounted samples to be retained by AM Lab. for future reference.

References

Crossley, D.W. (1967), The Bloomery at Rockley Smithies, Yorkshire. *Bulletin of the Historical Metallurgy Society*,**8**, 12-16.

Morton, G.W. and Wingrove, J. (1972) The Constitution of Bloomery Slags: Part II - Medieval. *J. Iron and Steel Inst.*, 210, 478-488.

APPENDIX I Full analysis of materials from Rockley Blast Furnace

AML ref.	Sample Area		C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni
Rock5/11/1	charcoal(C2:5)	elem%	49.6	ns	42.9	0.1	0.7	0.2	0.3	nd	0.2	nd	0.1	6.0	nd	nd	nd	nd	ns
Rock5/11/2		elem%	49.0	ns	43.0	0.3	0.9	0.1	0.1	nd	0.2	nd	0.0	6.4	nd	nd	nd	nd	ns
Rock5/11/3		elem%	47.3	ns	45.3	0.1	0.9	0.1	0.1	nd	0.2	nd	0.1	6.0	nd	nd	nd	nd	ns
Rock5/14/1	charcoal (C5a:43)	elem%	50.7	ns	42.9	0.1	0.5	0.1	0.2	nd	0.1	nd	nd	5.4	nd	nd	nd	nd	ns
Rock5/14/2		elem%	48.1	ns	42.0	0.7	0.4	0.2	0.4	nd	1.2	nd	nd	6.6	nd	nd	nd	0.3	ns
Rock5/14/3		elem%	49.7	ns	43.3	nd	0.5	0.2	0.3	nd	0.2	nd	nd	5.6	nd	nd	nd	nd	ns
Rock5/10/1	coke (C20:35)	elem%	72.1	ns	18.2	nd	nd	1.1	1.3	nd	1.8	nd	0.2	1.0	nd	nd	nd	4.1	ns
Rock5/10/2		elem%	77.3	ns	17.0	nd	nd	1.0	1.1	nd	1.4	nd	0.2	0.7	nd	nd	nd	1.4	ns
Rock5/10/3		elem%	80.3	ns	14.2	nd	nd	0.3	0.4	nd	1.7	nd	nd	0.9	nd	nd	nd	2.2	ns
Rock5/13/1	coke (C16:2)	elem%	65.8	ns	25.9	nd	nd	1.1	1.2	nd	1.4	nd	nd	1.3	nd	nd	nd	3.2	ns
Rock5/13/2		elem%	74.9	ns	16.1	nd	nd	0.5	0.6	nd	2.1	nd	nd	1.1	nd	nd	nd	4.6	ns
Rock5/13/3		elem%	54.6	ns	31.3	nd	nd	1.6	2.1	nd	1.2	nd	0.5	4.3	0.3	nd	nd	4.0	ns
Rock5/5/1	ore (C18:2)	elem%	7.2	ns	41.7	nd	1.7	3.6	8.4	nd	nd	nd	0.8	2.6	0.2	nd	0.6	33.4	nd
Rock5/5/2		elem%	6.4	ns	42.8	nd	1.5	5.7	9.7	nd	nd	nd	0.9	2.3	0.2	nd	0.5	29.9	nd
Rock5/5/3		elem%	7.1	ns	41.2	nd	1.6	3.1	10.1	nd	nd	nd	0.7	2.4	0.1	nd	0.6	33.1	nd
Rock5/5/4		elem%	4.9	ns	45.0	nd	1.3	7.1	14.9	nd	nd	nd	1.5	2.0	0.2	nd	0.2	22.8	nd
Rock5/5/5		elem%	5.5	ns	44.4	nd	1.3	5.7	13.7	nd	nd	nd	1.1	2.1	0.2	nd	0.3	25.7	nd
Rock5/6/1	ore (C5:31)	elem%	9.1	ns	36.8	nd	nd	2.8	8.4	nd	nd	nd	0.6	nd	nd	nd	nd	42.4	nd
Rock5/6/2		elem%	9.2	ns	36.4	nd	nd	3.6	6.7	nd	nd	nd	1.1	nd	0.5	nd	nd	42.5	nd
Rock5/6/3		elem%	9.3	ns	36.5	nd	nd	3.2	6.7	nd	nd	nd	0.7	nd	0.2	nd	nd	43.3	nd
Rock5/6/4		elem%	9.2	ns	34.0	nd	1.1	2.9	6.4	nd	nd	nd	0.7	2.4	nd	nd	0.4	42.7	nd
Rock5/6/5		elem%	8.7	ns	37.4	nd	nd	2.5	10.1	nd	nd	nd	0.5	0.3	nd	nd	nd	40.4	nd
Rock5/9/1	limestone (C18:12)	elem%	10.8	ns	51.3	nd	0.3	0.4	1.1	nd	nd	nd	nd	35.8	nd	nd	nd	0.3	nd
Rock5/9/2		elem%	10.7	ns	51.5	nd	0.3	0.4	1.2	nd	nd	nd	nd	35.8	nd	nd	nd	0.2	nd
Rock5/9/3		elem%	10.5	ns	52.4	nd	0.3	0.3	1.0	nd	nd	nd	nd	35.2	nd	nd	nd	0.3	nd

AML ref.	Sample	Area		C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni
Rock5/1/6	slag (C1:15)		oxide%	ns	ns	ns	nd	7.1	18.5	42.4	nd	nd	ns	3.5	18.9	0.9	nd	4.0	4.8	nd
Rock5/1/7			oxide%	ns	ns	ns	nd	7.0	18.3	42.5	nd	nd	ns	3.5	18.5	0.8	nd	3.8	5.6	nd
Rock5/1/8			oxide%	ns	ns	ns	nd	7.1	18.6	42.7	nd	nd	ns	3.4	18.7	0.9	nd	3.8	4.8	nd
Rock5/2/6			oxide%	ns	ns	ns	nd	7.1	18.5	42.5	nd	nd	ns	3.2	18.6	0.9	nd	3.9	5.4	nd
Rock5/2/7			oxide%	ns	ns	ns	nd	6.9	17.7	41.9	nd	nd	ns	3.5	19.4	0.9	nd	4.1	5.7	nd
Rock5/2/8			oxide%	ns	ns	ns	nd	7.2	18.6	42.2	nd	nd	ns	3.4	18.4	0.9	nd	3.8	5.5	nd
Rock5/2/9			oxide%	ns	ns	ns	nd	6.9	18.2	42.7	nd	nd	ns	3.6	18.7	1.0	nd	3.8	5.2	nd
Rock5/2/10			oxide%	ns	ns	ns	nd	6.8	18.7	42.9	nd	nd	ns	3.4	18.8	0.8	nd	3.6	5.1	nd
Rock5/4/1	slag (C5:29)		oxide%	ns	ns	ns	nd	6.9	18.3	42.3	nd	nd	ns	3.4	18.3	1.0	nd	4.0	5.7	nd
Rock5/4/2			oxide%	ns	ns	ns	nd	6.5	18.2	43.5	nd	nd	nd	3.3	18.8	0.7	nd	3.7	5.2	nd
Rock5/4/3			oxide%	ns	ns	ns	nd	7.0	18.1	41.9	nd	nd	nd	3.2	18.7	0.9	nd	3.8	6.3	nd
Rock5/4/4			oxide%	ns	ns	ns	nd	6.7	18.1	42.3	nd	nd	nd	3.2	18.3	0.8	nd	3.6	6.6	nd
Rock5/4/5			oxide%	ns	ns	ns	nd	7.0	18.2	43.2	nd	nd	nd	3.2	18.4	0.9	nd	3.8	5.2	nd
Rock5/12/4	slag (C15:76)		oxide%	ns	ns	ns	nd	4.2	22.4	40.1	nd	nd	nd	3.1	0.7	1.0	nd	0.8	27.6	nd
Rock5/12/5			oxide%	ns	ns	ns	nd	2.4	21.1	56.3	nd	nd	nd	3.1	1.2	1.2	nd	0.4	14.2	nd
Rock5/12/6			oxide%	ns	ns	ns	nd	2.0	19.9	53.9	nd	nd	nd	4.0	0.8	1.4	nd	0.4	17.7	nd
Rock5/7/1	casting	bulk	oxide%	ns	ns	ns	nd	5.3	14.6	43.5	nd	nd	nd	2.8	17.9	0.7	nd	2.8	12.4	nd
Rock5/7/2	sand/		oxide%	ns	ns	ns	nd	2.8	9.5	66.7	nd	nd	nd	2.1	10.0	0.6	nd	1.4	6.9	nd
Rock5/7/3	slag		oxide%	ns	ns	ns	nd	1.6	6.9	80.1	nd	nd	nd	2.2	6.2	0.3	nd	0.9	1.8	nd
Rock5/7/4		quartz incusion	oxide%	ns	ns	ns	nd	nd	0.1	98.2	nd	nd	nd	nd	nd	nd	nd	nd	1.7	nd
Rock5/7/5		glassy matrix	oxide%	ns	ns	ns	nd	4.7	13.8	58.3	nd	nd	nd	2.2	15.5	0.6	nd	2.3	2.5	nd
Rock5/7/7			oxide%	ns	ns	ns	nd	5.3	14.7	44.3	nd	nd	nd	2.9	17.6	0.7	nd	2.8	11.7	nd
Rock2/19	Chisel	iron matrix	elem%	ns	ns	ns	nd	nd	0.1	0.1	nd	nd	0.0	nd	nd	nd	nd	nd	99.8	nd
Rock2/2		inclusion	oxide%	ns	ns	ns	nd	nd	3.2	18.1	2.3	nd	ns	1.5	4.3	nd	nd	1.9	68.7	nd
Rock2/3		inc.mid grey phase	oxide%	ns	ns	ns	nd	nd	1.3	27.1	1.7	nd	ns	0.8	3.5	nd	nd	3.3	62.3	nd
Rock2/4		inc.white phase	oxide%	ns	ns	ns	2.1	nd	11.0	27.9	6.8	nd	ns	4.8	12.4	nd	nd	1.4	33.5	nd
Rock2/5		inc.mottled phase	oxide%	ns	ns	ns	nd	nd	1.1	2.9	0.3	nd	ns	0.2	0.7	nd	nd	1.2	93.6	nd
Rock2/6		inclusion	oxide%	ns	ns	ns	nd	1.4	3.0	33.0	nd	nd	ns	1.7	8.4	nd	nd	30.4	22.2	nd
Rock2/7		inclusion	oxide%	ns	ns	ns	nd	2.3	3.8	44.1	nd	1.2	ns	1.8	9.2	nd	nd	28.0	9.5	nd
Rock2/8		inclusion	oxide%	ns	ns	ns	0.7	0.9	2.5	18.1	4.2	nd	ns	1.2	3.8	nd	nd	2.8	65.9	nd
Rock2/9		inclusion	oxide%	ns	ns	ns	1.1	1.7	5.5	44.6	nd	nd	ns	2.8	9.0	nd	nd	3.7	31.7	nd
Rock2/10		inclusion	oxide%	ns	ns	ns	0.6	1.5	3.9	38.9	nd	0.7	ns	2.0	8.6	nd	nd	28.1	15.8	nd
Rock2/12	Chisel	inclusion	oxide%	ns	ns	ns	nd	2.0	3.3	45.8	nd	1.1	ns	1.6	10.4	nd	nd	30.2	5.6	nd

AML ref.	Sample	Area		C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni
Rock2/13		inclusion	oxide%	ns	ns	ns	0.6	0.3	3.1	59.7	nd	nd	ns	1.7	3.6	nd	nd	3.4	27.7	nd
Rock2/14		inclusion	oxide%	ns	ns	ns	1.2	0.6	4.3	21.5	7.0	nd	ns	2.5	5.6	nd	nd	2.6	54.8	nd
Rock2/15		inclusion	oxide%	ns	ns	ns	1.5	0.5	2.8	28.3	3.0	0.4	ns	1.3	4.2	nd	nd	2.1	55.8	nd
Rock2/16		inclusion	oxide%	ns	ns	ns	0.4	2.0	2.7	37.6	0.3	0.4	ns	1.2	8.4	nd	nd	28.3	18.7	nd
Rock4/18	weigh	steel matrix	elem%	ns	ns	ns	nd	nd	0.1	0.3	nd	nd	nd	nd	nd	nd	nd	0.4	99.2	nd
Rock4/19	beam	iron matrix	elem%	ns	ns	ns	nd	nd	0.1	0.1	nd	nd	0.1	nd	nd	nd	nd	nd	99.8	nd
Rock4/5	part	inc. in iron	oxide%	ns	ns	ns	nd	nd	nd	7.1	1.9	nd	ns	nd	nd	nd	nd	1.5	89.4	nd
Rock4/6		inc. in iron	oxide%	ns	ns	ns	nd	nd	nd	11.0	7.7	1.6	ns	nd	nd	0.4	nd	1.1	78.3	nd
Rock4/7		inc. in iron	oxide%	ns	ns	ns	nd	nd	2.1	16.7	4.3	0.8	ns	nd	0.4	0.6	nd	2.8	72.3	nd
Rock4/8		inc. in iron	oxide%	ns	ns	ns	nd	nd	1.5	8.4	3.8	nd	ns	nd	0.4	nd	nd	1.4	84.6	nd
Rock4/9		inc. in iron	oxide%	ns	ns	ns	nd	nd	0.9	11.3	7.9	nd	ns	nd	0.5	nd	nd	1.3	78.1	nd
Rock4/10		inc. in steel	oxide%	ns	ns	ns	nd	nd	2.5	73.1	nd	0.3	ns	nd	nd	0.3	nd	6.0	17.8	nd
Rock4/12		inc. in steel	oxide%	ns	ns	ns	nd	nd	2.4	76.3	nd	nd	ns	nd	nd	nd	nd	4.7	16.6	nd
Rock4/13		inc. in iron	oxide%	ns	ns	ns	nd	nd	nd	17.4	9.0	nd	ns	nd	0.5	nd	nd	2.1	71.1	nd
Rock4/14		inc. in iron	oxide%	ns	ns	ns	nd	nd	nd	3.0	2.3	nd	ns	nd	0.2	nd	nd	0.9	93.6	nd
Rock4/15		inc. in iron	oxide%	ns	ns	ns	nd	nd	2.3	18.3	5.1	0.8	ns	nd	0.3	0.4	nd	4.9	68.0	nd
Rock4/16		inc. in iron	oxide%	ns	ns	ns	nd	nd	nd	11.7	10.5	1.2	ns	nd	0.4	0.1	nd	1.7	74.4	nd
Rock4/17		weld inc.	oxide%	ns	ns	ns	nd	nd	nd	1.3	nd	nd	ns	nd	nd	nd	nd	0.7	98.0	nd
Rock3/12	Pig	iron matrix	elem%	ns	ns	ns	nd	nd	0.1	0.4	0.9	0.2	0.1	nd	nd	nd	nd	0.6	97.8	nd
Rock3/3		inclusion	elem%	0.0	ns	nd	nd	nd	nd	nd	nd	35.7	nd	nd	nd	nd	ns	64.3	nd	nd
Rock3/5		inclusion	elem%	0.0	ns	nd	nd	nd	nd	nd	nd	35.8	nd	nd	nd	nd	ns	64.2	nd	nd
Rock3/6		inclusion	elem%	ns	17.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	78.5	ns	nd	4.5	nd
Rock3/7		inclusion	elem%	ns	17.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	77.8	ns	nd	4.5	nd
Rock3/8		inclusion	elem%	0.0	ns	nd	nd	nd	nd	nd	1.6	29.0	nd	nd	nd	nd	ns	57.3	12.1	nd
Rock1/14	Ladle	iron matrix	elem%	ns	ns	ns	nd	nd	nd	0.5	nd	nd	nd	nd	nd	nd	19.2	1.6	78.7	10.4
Rock1/5		inclusion	oxide%	ns	ns	ns	nd	nd	34.4	38.9	nd	3.4	ns	nd	nd	1.3	5.8	nd	16.2	nd
Rock1/6		inclusion	oxide%	ns	ns	ns	4.2	2.8	8.5	26.6	1.4	9.5	ns	1.8	17.7	1.2	5.2	0.4	20.7	nd
Rock1/7		inclusion	oxide%	ns	ns	ns	nd	nd	7.8	35.2	nd	nd	ns	nd	nd	nd	18.1	37.9	1.0	nd
Rock1/8		inclusion	oxide%	ns	ns	ns	nd	nd	nd	36.3	nd	0.8	ns	nd	nd	nd	17.0	45.9	nd	nd
Rock1/9		inclusion	oxide%	ns	ns	ns	nd	nd	9.4	7.2	nd	nd	ns	nd	nd	nd	51.3	32.1	nd	nd
Rock1/10		inclusion	oxide%	ns	ns	ns	nd	nd	8.0	42.5	nd	nd	ns	nd	nd	nd	5.9	43.6	nd	nd

ns = not sought

nd = not detected