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The exploitation of manganese-rich 'ore' to smelt iron in Mwenge, western Uganda, from the mid second millennium AD

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Abstract

By the later second millennium AD, iron production was a key economic industry in western Uganda, and Mwenge was a prominent centre of production, highly regarded for the quality of the iron it produced. Between 2007 and 2011, excavation and analysis of iron production remains from six smelting sites in Mwenge enabled the reconstruction of local smelting technologies in operation there from the fourteenth century AD onwards. Chemical and microstructural analysis of approximately 100 samples revealed that slag from some of these sites is typically characterised by a bulk chemistry high in manganese oxide (up to 12wt%) and knebelitic olivines. Slag samples from the remainder of the sites contain low levels of manganese oxide (below 4wt%) and fayalitic olivines. The majority of the slag samples also contain notable levels of phosphorous (1-2wt%).

This sample set provided an opportunity to discuss the impacts of manganese and phosphorous on the smelting systems in operation in Mwenge. Principal component analysis suggests that smelters in this region were deliberately combining an iron ore with a separate manganese-rich flux, rather than using a naturally manganiferous iron ore. This use of two 'ores' has parallels with ethnographic literature from the region, which link the use of a second ore to the production of a harder metal. It is believed that this is the first analytically documented example of the use of a manganese-rich flux in sub-Saharan Africa. In the absence of analyses of surviving iron artefacts, the data also provides an opportunity to consider the quality of the iron metal that would have been produced.

Keywords

Bloomery iron

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Slag

Manganese

Phosphorous

Uganda

Africa

Highlights

- Bloomery iron smelting in western Uganda produced manganese-rich slag
- Analysis suggests the use of a manganese-rich flux in addition to an iron ore
- Ethnographic data from the area reports the smelting of two combined ores
- Adding a Mn-rich flux may have positively impacted on the smelts
- Phosphorous levels were also noteworthy

1. Introduction

Many European iron ores are manganiferous (most commonly limonites, goethites and siderites; less frequently haematites and magnetites), of which there are significant deposits in the UK, France, Italy, Germany, Austria, Scandinavia and eastern Europe (Tylecote 1962; Rostoker and Bronson 1990: 46; Tizzoni and Tizzoni 2000; Verna 2001). Although manganese-rich slag – defined by Pleiner (2000: 252) as exceeding 3.5wt% MnO – is comparatively rare in the archaeological record (Hauptmann 2007), several examples of bloomery smelting of manganiferous ores come from these regions (e.g. Tylecote 1962, 1992; Straube 1996; Photos-Jones et al. 1998; Heimann et al. 2001; Buchwald 2003; Cech 2008a; Charlton et al. 2010; Crew et al. 2011; cf. references in Leroy et al. 2012).

Iron deriving from these manganese-rich iron ores was highly regarded for its superior qualities, including the famous Noric steel (Cech 2008b; see also Starley 1999 for an example of manganese-enriched high bloomery iron (stückofen process) used for the production of armour). As an alloying constituent with iron, manganese is believed to encourage the uptake of carbon (increasing hardenability) and nitrogen (increasing strength, hardness, hardenability and resistance to corrosion) and remove sulphur (reducing hot shortness) (Rostoker and Bronson 1990: 99; Charlton 2007: 106-108; Crew et al. 2011). However, the role of manganese in bloomery iron is yet

to be fully understood, particularly in terms of whether the transfer of manganese to iron metal is feasible in bloomery furnace conditions.

Manganiferous iron ores are thought to be far less common in tropical and semitropical regions than in Europe. Manganiferous limonites and siderites are said to be “almost entirely absent” from sub-Saharan Africa, with “scattered occurrences” of high manganese haematites (Rostoker and Bronson 1990: 46). Although it is possible that this apparent scarcity may reflect an incomplete geological knowledge of the African continent, it does seem to correlate with the rarity of recorded smelting that utilised manganese-rich iron ores in Africa. Cline (1937), in his gazetteer of African smelting, makes only a single reference to such a technology. The ore used in Aoumbo, southern Gabon contained c. 70wt% iron oxide and 8wt% manganese oxide (Cline 1937: 43). Limonite ores smelted in southern Ethiopia contained between 2 and 4wt% (Todd and Charles 1978).

The research presented here adds a further African example of bloomery smelting using a manganese-rich charge (Iles 2011). Analysis of slag from six iron smelting sites in Mwenge, western Uganda revealed manganese oxide levels ranging up to 12wt%. However, the slag chemistry indicates that high-manganese slag is only typical at three of the six sites, correlating broadly with sites dating to the later second millennium. The remainder of the sites contain slag with a maximum of 4wt% manganese oxide. This scenario provided an opportunity for focused discussion on the behaviour of manganese oxide within iron smelting systems, its impact on smelting outcomes, and the possible addition of a separate manganese-rich flux to the smelts, rather than the use of a manganiferous iron ore.

2. New research in Mwenge

Unlike other areas of the Great Lakes (e.g. van Noten 1979, 1983; van Grunderbeek et al. 1983; Schmidt and Childs 1985; Humphris 2010), evidence for early iron production (i.e. pre-1000 AD) in western Uganda is currently lacking, with the earliest iron production presently recorded at around the 14th century AD (Robertshaw 1997; Iles 2013). Once established in the region, iron production played a prominent role in the later history of western Uganda and the growth of the kingdom of Bunyoro, with iron becoming a cornerstone of industry, regional trade and social

power through the second millennium AD. Mwenge, located towards the southwest extent of the kingdom's control (Figure 1), is reputed to have been one of the most prolific iron producing areas of western Uganda (Buchanan 1974; Doyle 2000).

A series of interviews carried out in 1994 and 1995 documented the smelting technologies operational in Mwenge within living memory (Childs 1998a, 1998b, 1999, 2000). These relatively recent examples of smelting recorded the use of two ores called entabo and obutale in the local Lunyoro/Rutoro language: one described as hard and black, the other as soft and red. Nevertheless, prior to the fieldwork on which this paper is based, a dedicated archaeological study of Mwenge's iron metallurgy had yet to be undertaken (Tosh 1970; Robertshaw 1994).

In 2007, intensive archaeological survey was carried out in order to identify sites relating to iron production, covering an area of Mwenge of about 40km by 40km (Figure 2). The survey was immediately followed by excavation at six smelting sites, including excavation of extant furnace remains and sampling of slag blocks associated with these furnace sites. The total volume of slag remains varied widely from site to site, but none of the excavated sites incorporated large and defined slag heaps. Instead, the slag tended to have been moved to the edge of household farming plots where it formed small piles. It is estimated that each of the sites discussed here contained a maximum of between 50 and 100 slag blocks. This relatively low volume of extant slag is likely to be related at least in part to the widespread practice of reusing slag blocks as a construction material (Iles 2011).

All excavated furnaces were found to be pit furnaces with diameters of c. 50-100cm, ranging in depth from c.30-60cm (Iles et al. 2014). A single C14 date was obtained from charred wood and grasses from the lower furnace fill of each excavated furnace (Table 1). All C14 samples were found to date to the 2nd millennium AD: three cluster in the 14th and early 15th centuries (Kyakaturi, Rugombe, Mironko); three date broadly to the 17th to 20th centuries (Kironko, Kisamura, Rukomero). These dates provide a time frame for the operation of the individual furnaces themselves, but cannot be said to be representative of the total operational period of the sites nor directly related to the sampled slag blocks. The full results of the survey and excavation are reported elsewhere (Iles 2009a, 2011, 2013).

Complete, unfractured slag blocks were frequently encountered, often reflecting the shape and configuration of the furnace from which they derived. All slag is non-tapped iron smelting slag. Impressions of small to medium reeds and grasses were present in and on most blocks, especially on the lower portions of the slag blocks. Very occasionally, sedge impressions with a triangular-profile were also apparent, as well as impressions of *Musa* species. Internal diameters (bore hole size) of tuyères measured on average 4.4cm, typical for tuyères fed by bellows. The continuous, parallel, longitudinal striations visible along many of the interior surfaces of the tuyères suggests that they were formed around a stick. This practice has been widely documented ethnographically (e.g. Todd and Charles 1978; Schmidt 1997).

Samples of slag, tuyère, and where possible furnace lining, domestic pottery and potential ore samples were collected from all excavated sites. Macroscopic descriptions, dimensions and detailed notes were recorded of all slag and tuyère samples prior to sample preparation. Sub-sets of typical and atypical samples were selected for analysis, aiming for a balanced representation of the assemblage in the final sample set (Orton 2000: 30). In total, 72 samples of slag, 23 samples of ceramic and 10 samples of ore and other related materials were sampled for polarizing energy dispersive X-ray fluorescence analysis (PED-XRF). This represents on average c. 10% of the available slag assemblage at each smelting site. 58 of these were also examined by reflected light microscopy, of which 27 were subject to microanalysis using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). In 2013, a further sample of ore – identified as entabo – was provided by P. Robertshaw for analysis. This sample had been collected during fieldwork in 1991 from a town called Kigugu, approximately 2km from the excavated site of Kirongo. A polished thin section of this sample was prepared for transmitted light microscopy and microprobe analysis.

3. Analytical methods

3.1 Microscopy

For optical microscopy and SEM-EDS analysis, resin-mounted polished blocks were prepared following standard procedures. Samples were set in a two-part epoxy resin, then ground and polished to a grade of 0.25µm. A thin section was prepared of the

sample of entabo to a thickness of 30 μ m, and highly polished to a standard suitable for electron probe microanalysis (EPMA).

A Hitachi S-3400N scanning electron microscope with an Oxford Instruments EDS was utilised at the UCL Institute of Archaeology, London, at an accelerating voltage of 20kV and a working distance of 10mm. INCA analytical software was used to translate the measured spectra into compositional data of weight percentages, presented as oxides calculated by stoichiometry. To ensure continued quantitative reliability, calibration of the EDS was undertaken at 30 minute intervals using a cobalt standard. Results were normalised to 100% to account for internal sample porosity and small variations in beam intensity. Detection limits were generally below 0.5%, excepting Zr (1.7%). Three basalt standard reference materials with published compositions (BHVO-2, BIR-1 and BCR-2) were analysed under the same conditions as the samples (U. S. Geological Survey Geochemical Reference Materials and Certificates 1988; cf. Iles 2011). The mean analytical errors for major elements present above c. 10wt% ranged between c. 1% relative (Fe) and 7% relative (Al).

EPMA was undertaken on the sample of entabo at the Department of Space Sciences, University of Arizona, using a Cameca SX100 electron probe microanalyser. Calibration standards for Mg, Al, Na, Si, Ca, P, Mn, Fe, Ba, K and Ti were used. The beam was operated at 15kV, with beam current of 20nA. Detection limits were generally around 0.1wt% or lower. Elements were converted to oxides by stoichiometry. Analytical totals were relatively low, ranging between 91.61 and 99.26 wt%. This reflects the variable valences of manganese in the manganese oxides of the sample minerals, and the presence of hydroxides.

3.2 Bulk chemical analysis

Compressed powder pellets were prepared for PED-XRF analysis. 15-20 grams of representative material were removed per sample, avoiding areas of slag bearing visible corrosion products, and avoiding ceramic that displayed vitrification. These were crushed and pulverised to a grain size of less than 50 μ m. The sample powders were mixed with a wax binding agent and compressed in a hydraulic press.

A Spectro Lab XPro 2000 instrument was used with five secondary targets at UCL Institute of Archaeology, run with an evaluation programme suited to the analysis of iron-rich materials (Veldhuijzen 2003) and calibrated for use with compressed pellets. To assess precision, three measurements were taken from each sample, which were averaged to give the reported value. Major and trace elements were converted to oxides by stoichiometry, and the results normalised to 100%. In order to check the accuracy of the results, three standard reference materials were analysed alongside each type of sample (BCS 301, ECRM 681, and Swedish Slag (Kresten and Hjärthener-Holdar 2001; Paynter 2006) for slag and ore samples (cf. Table 2); SARM 69, NIST 76a and ECRM 776 for ceramic samples). Average accuracy across the three measured reference materials was typically better than 6% relative for oxides at concentrations above 10wt% in the slag and ore samples. Silica was the only problematic compound, with consistent overestimations ranging between 10 and 27% in samples with low silica content (i.e. slag and ore), effecting changes in estimated composition of up to around 4wt%. In order to compensate for this, silica levels in the slag and ore samples were adjusted empirically on a sliding scale after normalisation (cf. Iles 2011).

3.3 Principal Component Analysis

Principal component analysis (PCA) was chosen as a tool by which to identify and interrogate chemical clustering within the slag dataset. Data were manipulated in Microsoft Excel and analysed in SPSS v22. The PED-XRF analyses for all slag samples, as presented in Table 2, were normalised to iron oxide prior to PCA in order to eliminate the partition effect of iron between the slag and the bloom. Na and S were excluded from the analyses. Measurements below the limit of detection (occurring within Mg, Ti, V, Co, Ni, Zn, Se, Y and Nd) were replaced with zeros. It is accepted that replacement of measurements below detection limits with zeros can distort the outputs of PCA (cf. Charlton et al. 2012). However, the alternative – replacing such measurements with the minimum value recorded in the same slag group – was not always possible in this instance, as for some elements (e.g. Co) no values were detected at all within certain slag groups. Those elements with a large proportion of measurements below detection limits, and which were also not considered critical to an understanding of the variation within the slag dataset – Ni, Zn and Se – were excluded from the PCA.

4. Results

Principal component analysis was performed as described on the bulk chemical data of all slag samples in order to summarise the relationships between the slag samples and their chemical compositions. Manganese and barium oxides were found to have very similar heavy loadings for principal component 2 (PC2), and showed a negative correlation with titania and cobalt oxide (Figure 3). Slag deriving from the sites of Kyakaturi (KTR) and Rukomero (RKM) formed coherent, distinct groups in the area of the loading plot associated with low manganese and low barium compositions. Some samples from Mirongo (MNGa-h) and Rugombe (RGBa-d) also fall within this area, but are more dispersed. The slag from Kirongo (KRG), Kisamura (KSM) and the remaining samples from Mirongo and Rugombe were concentrated in the upper left quartile of the bi-plot, characterised by manganese and barium oxides.

The variation illustrated on the PCA bi-plot broadly separates the slag samples into two groups: those with a high manganese oxide / low iron oxide signature (40 samples, averaging 8wt% MnO and 50wt% FeO) versus those with a low manganese oxide / high iron oxide signature (32 samples, averaging 2wt% MnO and 58wt% FeO). The slag from the site of Mirongo separates into both manganese-poor (samples MNGa-h) and manganese-rich (samples MNGi-n), which derived from two distinct and separate areas of the site (Iles 2011). The manganese-poor samples were excavated from the furnace itself and its immediate area, and are thus considered to be more closely linked to the c. 14th-15th century AD date obtained from this site. The site of Rugombe also bore both manganese-rich and manganese-poor slag samples. These two chemical groups of slag – manganese-poor and manganese-rich – are presented and discussed separately below.

4.1 Manganese-poor slag (Kyakaturi (KTR), Rukomero (RKM), Rugombe (RGBa-d), Mirongo (MNGa-h))

The 32 manganese-poor slags contain on average 6wt% alumina, 26wt% silica, 2wt% manganese oxide (ranging between 1 and 4wt%) and 58wt% iron oxide (calculated as FeO, ranging between 43 and 76wt%). Of the manganese-poor samples, those from Kyakaturi contain the least manganese oxide, with under 1wt% on average, whereas slag from other sites tends to contain between 2 and 3wt% (Table 2). Phosphate is

notably and consistently high in all slag samples, ranging up to 4wt%, excepting those from Rukomero, where phosphate levels do not rise above 0.07wt%. All samples contain moderate levels of lime, rarely falling beneath 1wt%, but reaching almost 4wt% in some.

As well as barium oxide and some rare earth oxides, levels of cobalt, copper and zirconium oxides are notably high in these samples (Table 2). In the high temperature and strongly reducing atmosphere typical of an iron smelting furnace, these oxides tend to be reduced to their constituent metals (cf. Ellingham diagram, Gilchrist 1989). The more volatile metals would thence have evaporated (e.g. Zn, with a boiling point of 907°C), whilst those less volatile would have preferentially reduced into the iron metal rather than remain in the slag (e.g. Co, Cu) (Crew 2000; Desaulty et al. 2009). The fact that these metals remain in the slag in any quantity is testament to the high levels of them entering the smelt.

The microstructures of the manganese-poor slags tend to be dominated by fayalitic olivines in a glassy matrix (Figure 4). The fayalite is relatively pure Fe_2SiO_4 , with some substitution of manganese oxide (c. 1-5wt%), lime (c. 1-2wt%), and less commonly magnesia, for iron. The blocky fayalite structure in all the manganese-poor samples indicates a slow cooling rate for the slag throughout the smelt, including those samples taken from the base of a slag block, which suggests that even at the beginning of the smelt the slag did not drip into a cold furnace pit. The glassy matrices of these manganese-poor slags tend to be lime rich (c. 17wt%), with notable levels of phosphate (2-3wt%). Clusters of leucite (KAlSi_2O_6) were frequently observed growing out of the glass phases.

Occasional and very small pinkish spinels of magnetite (Fe_3O_4) hercynite (FeAl_2O_4) solid solution are present in these samples (Figure 5), with some Ti^{4+} and Mn substituting for Al. Microanalyses determined these phases to comprise on average 65wt% iron oxide, 30-35wt% alumina and 3wt% titania. These magnetitic hercynite spinels would have been one of the final residual phases to form as the slag solidified, and indicate that these slag blocks probably formed in conditions that were not strongly reducing.

Wüstite is generally rare in the manganese-poor samples, except in the iron-rich Mirongo slag, where wüstite comprises up to 70area%, correlating with the higher bulk iron oxide contents. Leucite-wüstite eutectic intergrowths were noted in these samples; occasional euhedral crystals of hercynite (FeAl_2O_4) and droplets of metallic iron are also present. Sample RGBb, with a bulk iron oxide content of 68wt%, also contains a relatively high proportion of wüstite (up to 30area%). The glassy matrix of this sample is unusually enriched in iron oxide (c. 30-50wt%) and phosphate (c. 17-45wt%). The high iron content of the matrix, as well as the prevalence of wüstite and corroded iron, accounts for the high levels of iron oxide in the bulk chemical analysis of this sample.

The liquidus temperatures of the manganese-poor slag samples were estimated by plotting the bulk chemical compositions of the samples on the $\text{FeO-SiO}_2\text{-Al}_2\text{O}_3$ ternary phase diagram (Figure 6). Plots were presented as $(\text{FeO}+\text{MnO}+\text{CaO})\text{-SiO}_2\text{-(Al}_2\text{O}_3+\text{TiO}_2)$, combining compounds that act to lower the melting temperature of the slag (MnO, CaO, FeO) and those that raise the melting temperature (TiO_2 , Al_2O_3). The majority of the samples fall securely within the region of the phase diagram that is associated with the formation of fayalite, consistent with the results of the microscopic analysis. Minimum operating temperatures of the furnaces from this group are estimated to have been in the range of around 1100 to 1200°C.

Bulk chemical analysis undertaken on samples of tuyère from Kyakaturi, Rugombe, Mirongo and Kisamura (tuyère fragments were absent from the sites of Rukomero and Kirongo) indicated that they had been formed from kaolinitic clays, containing on average 72wt% silica – reflecting the high levels of observed quartz – and approximately 22wt% alumina (Table 3). SEM-EDS analysis of the clay fabric from a tuyère from Mirongo (avoiding quartz and other inclusions) indicated an alumina content of c. 35wt% and a silica content of c. 55wt%. Refiring experiments on comparable technical ceramics by Freestone and Tite (1986: 41-46) suggest that such ceramics may have been capable of enduring temperatures of up to 1250°C. The refractory nature of these kaolinitic ceramics would have limited how much were consumed by the smelts, and it is unlikely that they would have contributed

significantly to the formation of the slag at the minimum operating temperatures suggested here.

Ores

A single fragment of unreduced ore with an iron oxide (FeO) content of nearly 90wt% was excavated from the furnace pit at Kyakaturi (KTR Ore, Table 3). Cobalt, zinc, lanthanum, cerium and neodymium oxides all registered very high readings in this sample, which could link this ore to the slag samples from the site. The relatively high level of P₂O₅ (c. 1.4wt%) also corresponds with the phosphate in the slag. However, the alumina to silica ratio of the ore sample is just over 1:1, whereas in the slag it is c. 1:4. It is thus possible that this piece of ore is not representative of the ore actually used at Kyakaturi. However, if it is, the low levels of associated gangue would have required a considerable contribution of silica from an alternative source in order for fayalite to form. This extra silica would have been unlikely to have derived from the ceramics, considering the refractory nature of the ceramics themselves.

An alternative possibility is the addition of a separate silica flux, and indeed a small fragment of a metamorphic quartzitic rock was also recovered from the furnace fill at Kyakaturi. This may be a remnant of an acidic flux that was added to the smelt in order to encourage the formation of a slag. The addition of quartzitic sand has been identified at Phalaborwa, South Africa (Miller et al. 2001), where rich magnetite ores with very little gangue were fluxed with sand from nearby riverbeds. If this was indeed also the case at Kyakaturi, the quartzitic rock would probably have been crushed or powdered before being added to the smelt, increasing the surface area relative to volume so that it could easily combine into the melt. The fact that this uncrushed fragment entered the smelt as a relatively large piece may have contributed to its survival in the furnace pit.

Several fragments of unreduced ore were also excavated from the furnaces at Rukomero. These measure a few cubic centimetres in size, are dark purplish black and often cracked. They vary considerably in quartz content, suggesting either that they had not been sorted thoroughly before inclusion in the smelt, or that these were discarded fragments thrown into the furnace after the completion of a smelt. Internal cracks, like those seen in roasted limonite ores used in Haya smelting (cf. Schmidt

1997: 114) were not visible through optical microscopy. The samples are strongly magnetic, perhaps magnetised through heating in the furnace. SEM-EDS analyses revealed a matrix of approximately 98wt% iron oxide, with approximately 0.5wt% of alumina and phosphate and just over 1wt% silica. Ill-defined areas enriched in alumina (of up to 13wt%) are also present, but these are very limited in size and frequency. PED-XRF analysis found these samples to contain up to 0.1wt% cobalt oxide, which would account for the levels of cobalt oxide in the slag samples from Rukomero (RKM Furnace 1 and 2 Ores, Table 3).

Haematite ore was also present at Rugombe, with iron oxide contents ranging between 62wt% and 93wt% and variable silica contents accounting for the difference. The porous nature of these minerals meant that they would have been readily penetrated by reducing gases within the furnace. Elevated levels of cobalt and copper oxides account for the raised levels of these compounds in the bulk chemical analysis of the slag blocks from this site.

4.2 Manganese-rich slag (Kirongo (KRG), Kisamura (KSM), Mirongo (MNGi-n), Rugombe (RGe-g))

The 40 manganese-rich slags typically contain an average of 8wt% alumina, 25wt% silica, 8wt% manganese oxide and 50wt% iron oxide (calculated as FeO, ranging between 35 and 58wt%, Table 2). Manganese oxide ranges between 3 and 12wt%, with variation within as well as between sites. Phosphate averages 1wt% across the sample set, ranging between 1 and 2wt%. Like the manganese-poor slags, these samples also contain moderate levels of lime, averaging 2wt% and ranging between 1 and 5wt%.

The iron oxide contents of these samples were lower than in the first group, particularly those from Mirongo, where levels range from 35 to 46wt%, with a mean value of 40wt%. Levels of silica and alumina are correspondingly raised. Barium levels are unusually high, measuring up to almost 4wt% in the samples from Mirongo, and 2wt% in samples from Kirongo, Rugombe and Kisamura.

The majority of the manganese-rich slags are dominated by olivines in a glassy matrix (Figure 7). There tends to be very little wüstite, consistent with the low iron oxide

contents of these slag samples (cf. Table 2). In many cases, wüstite is only present as tiny late-forming dendrites in the glass. The well-developed structure of the olivine phases throughout the slag blocks indicates that they did not cool quickly. However, the crystal sizes are relatively small, indicating a moderate cooling rate rather than a slow one. Microanalysis identified the olivines as knebelite $(\text{Fe,Mn})_2\text{SiO}_4$, containing between 12 and 38wt% manganese oxide. Lime is also present in the olivines of some samples, generally between 1 and 4wt%, but ranging up to 5 and even 13wt%. By acting as a substitute for iron oxide in the formation of olivines (in the case of lime, forming kirschsteinite $(\text{Ca,Fe})_2\text{SiO}_4$), both manganese oxide and lime free up more iron oxide to reduce to iron metal (see Discussion below).

Among the least frequently occurring phases in all samples are small euhedral crystals of hercynite and magnetitic-hercynite, often with substitution of Mn and other elements for Al, and often occurring within the olivines. Due to the higher melting point of the hercynitic phases, they would have crystallised before the knebelite, leaving the knebelite to accommodate them within it. Rarer still were occasional ulvitic phases with high alumina (12wt%) and manganese oxide (18wt%) in samples from Mirongo.

The samples from Kisamura are unusual in that they contain between 10 and 25area% dendritic wüstite as well as secondary late-forming wüstite in the glass. In many samples the wüstite had reduced to iron metal, resulting in metallic pseudomorphs of the wüstite dendrites from which they derived (Figure 8). The presence of iron even within samples taken from the very base of slag blocks is unusual, and might indicate a particularly reducing atmosphere, or an interruption in slag formation that allowed the wüstite in the previous slag accumulation to reduce to iron metal. Schmidt (1997: 119-124) noted similar features in Haya slag, which he interpreted to be the result of localised pockets of reducing conditions created by the charred grass filling the furnace slag pit. More likely, the slag may have been exposed to reducing furnace gases after dropping into the slag pit, enabling the top layer of the slag to reduce to metallic iron before the next slag layer dripped on top of it (cf. Iles and Martín-Torres 2009). Importantly, in this case, the phenomenon does not seem to indicate a highly viscous slag that would not separate from the bloom, but instead a continuation of metal reduction after the slag had dropped into the slag pit. Analysed wüstite

phases from Kisamura and Kirongo contained traces of manganese oxide of up to 14wt%, and titania up to 2wt%. Manganese and titanium were absent from analyses of metallic iron droplets within the samples, although they may have been present in concentrations below the detection limits of the EDS (approximately 0.26wt% and 0.17wt% respectively). Copper was detected at levels of up to 0.4wt%.

The liquidus temperatures of the manganese-rich slag samples were also estimated by plotting them on the FeO-SiO₂-Al₂O₃ ternary phase diagram in terms of (FeO+MnO+CaO)-SiO₂-(Al₂O₃+TiO₂) (Figure 9). The samples fit within a smaller compositional range than the slag samples considered in the preceding section, which might indicate a greater degree of regulation in smelting procedure at these sites. This is reflected in a comparison of the coefficients of variation (CV) of the bulk compositions of the manganese-rich slag samples and the manganese-poor samples, where the manganese-rich samples tended to have lower CVs (cf. Table 4).

Again, most samples fall in the fayalite region, or around the low temperature trough between fayalite and hercynite (note that the slag olivine is knebelite, with MnO added to FeO for the plots). The remainder of the samples plot within the alumina-rich area of the diagram, with a correspondingly slight rise in liquidus temperature. These samples were those from Kirongo, which tended to contain higher proportions of hercynite and magnetitic hercynite. As a whole, liquidus temperatures for these manganese-rich samples ranged between 1100 and 1250°C on this phase diagram. However, although this phase diagram has correctly predicted the phase formation in these samples, the high manganese oxide content may distort the estimation of solidification temperature. For comparison, the samples were also plotted on the FeO-MnO-SiO₂ phase diagram in terms of (FeO+CaO+alkalis)-(MnO)-(SiO₂+Al₂O₃). Most of the samples were located in the liquidus temperature range of 1200-1225°C (Figure 10), corresponding with the higher end of the liquidus temperatures derived from the FeO-SiO₂-Al₂O₃ phase diagram. Again, it is unlikely that the technical ceramics would have contributed much to the formation of the slag at these minimum operating temperatures. However, in those slag samples with bulk silica contents above c. 30wt% (including three samples from Kirongo and four from Mironko), the FeO-MnO-SiO₂ phase diagram suggests liquidus temperatures of up to c. 1400°C.

Ores

Two fragments of unreduced ore were excavated from the furnace pit at Kirongo. These were very hard, black and dense, with a metallic lustre suggestive of magnetite (Fe_3O_4). The bulk iron oxide (FeO) content of one of these samples is approximately 76wt%, with 6wt% titania and 12wt% manganese oxide (KRG Ore, Table 3). In reflected plane-polarised light, bluish inclusions criss-cross the sample (Figure 11), composed of titania (c. 55wt%) and manganese oxide (c. 40wt%), similar in composition to pyrophanite (MnTiO_3). The remaining ore matrix is primarily 78wt% FeO with significant manganese oxide and titania contributions. Taking into account the considerable level of titania in the analysed ore sample (c. 6wt%), it is surprising that there is not more titania present in the slag samples (c. 0.3wt%), particularly the furnace slag samples which are directly associated with it (cf. Iles and Martín-Torres 2009; Killick and Miller 2014). This may indicate that either the sample analysed is not representative of the ore selected for these smelts, or that this ore was combined with another with a lower titania content. Indeed, the alumina to silica ratio of this ore sample (1:0.8) does not correlate with that of the slag samples from this site (1:3.1).

Samples of two further possible ores were also excavated from a test pit at the site of Kisamura, which was situated approximately 2m to the southwest of the furnace base. Bulk analysis of these samples showed that neither was a viable iron ore. However, one of them, Ore B, with a very low iron oxide content of just under 20wt%, has a manganese oxide content of 23wt% (KSM Ore B, Table 3). It is possible that this, or a similar mineral, was the source of the manganese oxide in the slag samples from this site. If used as an ore or a flux, levels of zinc, barium and neodymium oxides, as well as lime and alumina in the bulk chemical analyses of the slag would also be accounted for. Equally, the relatively high nickel oxide content (c. 0.1wt%) apparent in this sample is not incongruous with its absence from the slag samples; nickel, like cobalt, is likely to partition completely into the forming iron bloom (Desautly et al. 2009).

5. Discussion

5.1 Manganese and iron: 'male' and 'female' ores

There are three possible scenarios that could result in the elevated manganese levels identified in some of the slag samples from Mwenge. The manganese may have

occurred naturally in association with the iron ore, it may have been added separately and deliberately to the ore mix, or it may have been present in the iron ore and in an additional fluxing material. The presence of elevated manganese oxide in slag has tended to be used as a stand-alone argument for the deliberate addition of a separate fluxing agent, although more commonly in relation to copper smelting rather than iron smelting (Hauptmann 2007: 181; although see Radivojevic et al. 2010 for an example of preferential selection of manganese-rich malachite rather than the addition of a manganese-rich flux). However, this relationship should not be assumed. One problem in distinguishing between these possibilities is because manganese and iron have similar chemical properties in the geological environment: the mineral forms of these elements often occur together in ore bodies (Rostoker and Bronson 1990). Iron ores in sedimentary deposits can be intergrown with manganese ores, effectively producing the qualities of a self-fluxing ore; it is often possible to explain a fluxing component as coming from the host rock of the ore itself. The manganese oxide levels in the slag samples from all Mwenge sites are relatively high (averaging 2wt% in the low-manganese slags), which strengthens the possibility that the variation in the manganese levels in the Mwenge slag reflects the utilisation of a variable Fe-Mn continuum ore body rather than the deliberate addition of a separate manganese ‘ore’ or flux.

However, in the case of western Uganda, the ethnographic data is suggestive of the use of a combination of two ores (Roscoe 1923; Childs 1998a): a ‘female’ ore described as red and soft (obutale), and a ‘male’ ore, described as black, glittery and hard (entabo). Without seeing the ores firsthand, Cline (1937: 117) interprets Roscoe’s description of the red, soft ore as haematite, and the hard, black ore as magnetite, yet the latter would also fit the description of a typical manganiferous mineral. Later research in the same area describes this entabo as “a dark, sand-like substance with some sparkling grains”, the addition of which was said to produce a positive effect on the resulting iron (Robertshaw 1991).

As such, in order to examine the hypothesis of whether two separate ‘ores’ – one iron rich, one manganese rich – were used, PCA of the complete slag dataset was undertaken, following the same methodology as previously outlined, but normalised to 100% (Table 5). This analysis illustrated a strong correlation between iron,

titanium, vanadium and cobalt oxides. These compounds had a negative correlation with those of a second group, comprising manganese, barium and neodymium oxides. As manganese can substitute for iron to form olivines in slag, thus enabling a greater proportion of iron oxides to reduce to iron metal (see Section 5.2), and because of the geological link between manganese and iron minerals, a direct negative correlation between manganese oxide and iron oxide in slag is to be expected. This correlation cannot therefore be used to identify whether or not iron oxide and manganese oxide are coming from the same source i.e. a single ore. Instead, this PCA of the slag dataset demonstrates the broader chemistry of the iron and manganese components: the iron oxide mineral occurs in association with titanium, vanadium and cobalt oxides; the manganese oxide mineral occurs in association with barium and neodymium oxides. It is significant to note that titanium and barium oxides – compounds that can derive from the ceramics (cf. Charlton 2006, Charlton et al. 2012) – do not occur in the analysed ceramic samples in levels high enough to account for the levels in the slag (cf. Table 3).

PCA was also applied separately to the manganese-rich and manganese-poor subsets of the PED-XRF data, normalised to iron oxide in order to achieve the clearest information about the initial gangue composition(s) in each subset (Tables 6 and 7). The strong correlations apparent in the manganese-poor slag samples suggest that fewer materials overall are contributing to these smelts (Table 6). Compounds associated with iron oxide – titanium, vanadium and cobalt oxides – continue to correlate, but this group now extends to include copper and chromium oxides. There remains a very strong correlation between manganese and barium oxides in these slag samples, but the negative correlation between the iron-related elements and the manganese-related elements has disappeared. This suggests that in these manganese-poor smelts, one ore was used: an iron ore with a Ti-V-Co-Cu-Cr signature, which occurred naturally with a minor manganese-barium component. In these samples, compounds associated with fuel-ash (cf. Charlton 2006; Charlton et al. 2012) – magnesia, potash and lime – show a clear and distinct correlation. The rare earth oxides and strontium, phosphorous and zirconium oxides also correlate particularly strongly, and demonstrate a consistent negative correlation with silica. These components are likely to be associated with a ceramic contribution to the slag formation. Minerals such as zircon ($ZrSiO_4$), monazite ($(Ce,La,Nd,Y)PO_4$) and

xenotime (YPO_4), occur as accessory minerals in granites and are highly resistant to weathering (D. Killick pers. comm. 2014). The strength of these particular correlations may be heightened due to a background geological signature that is present in contributions both from local ceramics and local ores (cf. Table 3).

In stark contrast to the manganese-poor samples, correlations in the manganese-rich slags are much weaker (Table 7), potentially reflecting higher dilution effects from a larger number of contributing components. The absence of a ceramic signature similar to that in these manganese-poor samples is intriguing, and may reflect the use of different clays in these smelts. Further analysis of a broader range of tuyère samples from these sites would be a preferred means to explore this. The strong correlation (0.75) between manganese and barium oxides in the manganese-poor samples diminishes to 0.39 in the manganese-rich samples, however the correlation between barium and neodymium oxides rises in the manganese-rich samples to 0.8. This may be indicative of a second source of manganese oxide being used in the manganese-rich smelts; when manganese oxide also enters the system from a second source with a different chemical signature, the correlation between manganese and barium oxides diminishes. These two sources most likely comprise an iron ore as before, which occurred naturally with a minor manganese-barium component, as well as a low-iron, high-manganese ‘flux’ with a barium-neodymium signature, as initially identified in the PCA analysis of the complete dataset (Table 5).

The apparent absence of titania and cobalt oxide from the slag samples with high manganese oxide may well be a further indication of the addition of a second mineral in these smelts. Neither TiO_2 nor V_2O_5 can be reduced within a bloomery furnace, so “both will transfer quantitatively to the slag during smelting” (Miller et al. 2001: 406). Co_3O_4 can be reduced during bloomery smelting, and cobalt’s siderophilic nature means it will partition, if only partly, to the iron (Desaulty et al. 2009). If present in the iron ores used in all sites, the dilution factor of adding a second manganese mineral at certain sites could render those compounds presumably coming predominantly with the iron ore – TiO_2 , V_2O_5 , Co_3O_4 – below the detection limits of the PED-XRF (or considerably lowered) in those instances. This might account for the variability in presence or “absence” of titania and vanadium oxide in the slag samples from, for example, the site of Kirongo (cf. Table 2).

The strong correspondence between barium and manganese oxides suggests that the mineral root is a hard, black psilomelane. The specific species of this mineral is likely to be the commonly occurring mineral romanèchite $(\text{Ba},\text{H}_2\text{O})_2(\text{Mn}^{4+},\text{Mn}^{3+})_5\text{O}_{10}$. The ratio of barium to manganese in Ore B from Kisamura (approximately 1:4.5) is close to the ratio of these compounds in the chemically pure form of this mineral (between 1:5 to 2:5, depending on water content). Recent analysis of a sample of entabo, collected in Kigugu (cf. Figure 2) in 1991 and provided by Pete Robertshaw for analysis in 2013, confirmed this hypothesis. Petrographic analysis found that garnet accounted for approximately 50% of the sample area (Figure 12), later confirmed by EPMA as spessartine $(\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3)$, potentially providing the source of the alumina levels identified in Kisamura Ore B. The remainder of the sample comprised intergrown manganese oxides, with varying contents of iron, magnesium and barium oxides and alumina (Table 8). As most manganese oxides occur as “intimately intermixed, fine-grained, poorly crystalline masses” (Post 1999: 3448), no attempt has been made to designate mineral species from these analyses. It is highly likely that the sample of entabo equates with the hypothesis of a manganese-rich material that was added to the later second millennium smelts at Kirongo, Kisamura, and used in some of the Mirongo and Rugombe smelts.

5.2 Manganese and iron: technical impacts

In Mwenge, it is said that “this substance [the entabo] was poured on the ore during smelting to produce a harder metal” (Robertshaw 1991). Having identified the entabo as a possible manganese flux, it was relevant to explore the technical impact of manganese oxide on bloomery smelting. The use of manganese as a desulphuriser, deoxidiser and alloy in historical and modern steel manufacture is widely discussed (e.g. Burt and Wilkie 1984; Truffaut 1994 among many others). However, manganese oxide’s role in bloomery smelting is less well understood, despite the fact that it has been credited with “radical improvement in metal quality” in modern experimental smelts (Sauder 2013: 73). The mechanisms of its positive effects may be ill defined, but they are probably the result of a combination of factors regarding how manganese oxide behaves within and impacts upon a smelt, with potential consequences for the iron that is produced.

Yield is often discussed as the primary impact of manganese on bloomery smelting. The presence of manganese oxide indeed has a beneficial effect in terms of the reduction efficiency of smelting systems on a purely chemical basis, maximising the return produced by a smelt as compared to materials put in (e.g. Crew and Charlton 2007; Charlton et al. 2010). Due to the chemical similarities manganese bears with iron, which it neighbours in the periodic table, manganese can replace iron to react with silica, forming knebelite $(\text{Mn,Fe})_2\text{SiO}_4$ rather than fayalite Fe_2SiO_4 . The replacement of Mn for Fe results in more free iron oxides within a given smelt that can reduce to metallic iron, increasing the percentage of metal that can be recovered from an iron ore (Tylecote 1962: 191; Rostoker and Bronson 1990: 19; Charlton et al. 2010). This effect was observed in the manganese-rich slag samples from Mwenge, the olivines of which contained levels of manganese oxide between 15 and 30wt%.

Hypothetical mass balance calculations from theoretical ore mixes – Fe-rich and mixed Fe-Mn – demonstrate this difference in maximum potential yield (Figures 13a, 13b, 13c). These basic mass balances assume that all silica is to be bound with either iron or iron and manganese to form fayalite or knebelite, and that all – or most – manganese oxide binds with silica in the knebelite. All remaining iron oxides are assumed to reduce to iron metal in the bloom. Knebelite is part of the continuous series between tephroite (Mn_2SiO_4) and fayalite (Fe_2SiO_4), and so the ratio of iron to manganese in the knebelite can vary considerably. As such two alternative Mn-Fe models were considered: one that mirrored the knebelite composition at Mirongo, samples MNGi-n $(\text{Mn}_1\text{Fe}_1)_2\text{SiO}_4$ (Figure 13b); and one that mirrored that at Kisamura and Kirongo $(\text{Fe}_{1.5}\text{Mn}_{0.5})_2\text{SiO}_4$ (Figure 13c). Other inputs and outputs are not accounted for. Although these systems are idealistic in real terms, they do serve to demonstrate the potential maximum proportion of iron ‘saved’ with the addition of manganese oxide. In theory, the proportion of iron recovered from these hypothetical ore mixes rose from 12% in the ore with 60wt% iron oxides (i.e. a 5kg bloom was recovered from a possible 42kg of available Fe in the original ore) to 39% and 30% in the examples with manganese oxide present. This is a considerable difference in potential yield, which is typically between 15 and 25% (David et al. 1989: 196). Similarly, Crew (2013) reports a yield of 32% from a manganese-rich bog iron ore, paired with a particularly low charcoal to ore ratio for the entire process from ore to iron bar.

If, however, manganese is enriched in an ore at the expense of iron oxides (rather than at the expense of alumina or silica), no yield benefit will be realised, as less iron oxide will be available for reduction (although the manganese-rich slag will appear leaner). On this basis, manganese is especially beneficial to a smelt if added separately, in addition to an iron-rich ore, and importantly may make the reduction of lower grade iron ores viable. However, discussions of yield often fail to consider the priorities of the smelter, assuming that yield is of paramount concern. A high yield (linked to a lean slag) is of little value to a smelter if the iron produced is unworkable or substandard. In Mwenje, ethnographic accounts emphasise the quality and ‘fit-for-purpose’ of iron and ores rather than the yield: “there are two classes of metal which they get from the iron ore: enyondo (this ore produces very tough metal) and ekibale (this ore is used for axes and spears, but it is not as tough)” (Buchanan 1974: 103).

In bloomery iron, the composition of the slag bath is critical to the ease with which the slag and bloom separate and the quality of the iron produced: a high-iron, “wustitey” slag is preferred (Espelund 1991; Photos-Jones et al. 1998; Sauder 2013: 72). However, the presence of manganese oxide has a similarly positive effect, fulfilling the same function of iron without iron being sacrificed to the slag. It provides flexible operating parameters, acting as a fluxing agent and deoxidiser for silica-rich gangue. It reduces the melting temperature of typical bloomery slag and weakens silicate bonds, encouraging a fluid slag that separates easily from the bloom at relatively low operating temperatures (Todd and Charles 1978). The low viscosity of manganese-rich slag means that it is also easily removed from the bloom at the forging stage (L. Sauder 2013 pers. comm.; see also Crew et al. 2011). Manganese-rich silicates are also tolerant of fluctuations in the furnace atmosphere (Hauptmann 2007): a smelt is less likely to ‘freeze’ at low temperatures even if the furnace atmosphere does not remain constant. Experiments with a mixed ore of iron (60wt%) and manganese oxides (10wt%) have demonstrated its highly reducible nature. With a fuel to ore ratio of 2:1, this manganese-iron mix was reduced very quickly to produce a bloom containing cast iron (Crew and Charlton 2007). The authors suggested that a much lower fuel to ore ratio, perhaps as low as 1:2, would have been sufficient to produce bloomery iron, thus lowering demands on charcoal production per volume of iron produced.

A bloomery furnace operating at a minimum temperature for iron smelting will theoretically not reduce manganese oxide to manganese metal, a process that requires a temperature of $>1400^{\circ}\text{C}$ at a CO/CO_2 ratio of 10^4 (Alcock 1976: 199-200; Rostoker and Bronson 1990: 19; Charlton 2007: 106). However, if conditions are exceptionally reducing, small amounts of manganese can reduce and partition to the metal in the production of cast iron (whether accidentally or intentionally, e.g. Tylecote 1962; Navasaitis and Selskiene 2007; Crew et al. 2011) or when conducive conditions are amplified at localised hot spots (Rostoker and Bronson 1990). It is therefore feasible that localised, carbon-contact manganese oxide reduction may occur within a bloomery furnace if temperature and reducing atmosphere are both relatively high. The presence of reduced iron in the manganese-rich slag from Mwenge (e.g. Figure 8) is testament to the fact that localised pockets of reducing conditions did occur, which may have enabled the partitioning of some manganese to the iron. Manganese reduction in the highly reducing *stückofen* process has been documented, resulting in iron with manganese contents averaging 0.04 wt% (Starley 1999).

Partitioning of manganese into bloomery iron at relatively low temperatures may also theoretically occur due to the absorption of manganese vapour (Rostoker and Bronson 1990). Manganese has a vapour pressure of 121Pa at a temperature of 1244°C , and although it may reoxidise in the lower temperatures higher up in the furnace or be discharged with other gases (Alcock 1976), some vapour may be absorbed by metallic iron. This is unlikely to result in a significant transfer of manganese to the iron, but it may account for the low levels of manganese ($<0.1\text{wt}\%$) seen in some archaeological samples of ironwork, such as the products of some early Roman and Hallstatt or La Tène bloomery smelting in modern Austria and Sweden (Coghlan 1977: 38; Rostoker and Bronson 1990: 20). Bloomery iron produced experimentally from southern Ethiopian limonites containing c. 4wt% MnO , appeared to contain between 0.05 and 0.2wt% manganese when reduced at 1200°C (Todd and Charles 1978), although some presumably would have reoxidised during smithing.

Although manganese is theoretically not likely to be reduced and alloy with iron in a bloomery furnace, it is frequently linked to a significant carburisation of iron. The production of Noric steel at Hüttenberger Erzberg, Austria has been attributed to the

exploitation of manganiferous limonite and siderite ores (Preßlinger 2008; Truffaut 2008). In iron-manganese steels, manganese has been found to increase the affinity of austenite for carbon (Darken 1949), however, within the bloomery furnace the mechanism by which manganese might encourage the uptake of carbon to iron is unclear, and at such low levels of manganese, any influence may be negligible. One possibility is the nature of manganese as a powerful reducing agent and catalyst. However, smelting with manganese-rich ores is thought to lower the critical CO_2 partial pressure mix needed to reduce a wüstite-olivine melt to metallic iron (Heimann et al. 2001). It is possible that this is due to the complex reaction kinetics of manganese oxides. Manganese oxides are highly active in reducing conditions, with potential implications for the atmosphere of the furnace. Forming strong bonds with oxygen in a number of valence states, manganese oxide will preferentially reoxidise (rather than iron or carbon) in temperatures analogous to that of a bloomery furnace. Furthermore, some studies have found manganese oxides to deviate from the stoichiometric ratios of their formulas, containing significant excess oxygen in air (Le Blanc and Wehner 1934; Davies and Richardson 1959; although see Hahn and Muan 1960 and Stobbe et al. 1999). The reduced CO_2 partial pressure of the CO_2/CO gas mix not only protects the forming iron from reoxidising (Truffaut 1994), it also affords an environment within which carbon can bond with, and remain bonded with, iron metal. Furthermore, it has been suggested that the exothermic nature of these oxidation reactions contributes to an elevated furnace temperature, further encouraging a clean separation of slag from the bloom (Stobbe et al. 1999; Crew et al. 2011).

SEM-EDS analyses of wüstite in slag samples from the manganese-rich sites in Mwenge averaged between 5 and 10wt% MnO. SEM-EDS analyses of droplets of iron within the slag however, were unable to detect any manganese, although it is probable that if present it would have been below the detection limits of the EDS (c. 0.18wt%). Without any analyses of bloom fragments or metal products from this region it is difficult to deduce whether the smelting of manganese-rich ores (or ore mixes) in this region would have made an impact on the resulting metal, whether in terms of manganese or carbon as alloying agents to the iron.

5.3 Phosphorous and iron

The second element of significance in the Mwenge slag samples was phosphorous, which like manganese, may have had a significant effect on the outcome (if not the operation) of the smelting system. Phosphorous, like carbon, greatly increases the strength of bloomery iron and improves its work hardenability, and results in a bloom that forges well (Sauder 2013). At concentrations of approximately 0.5wt%, phosphorous-rich iron acquires the strength and hardness of a medium carbon steel (Rostoker and Bronson 1990). However, at the same time it can make iron lose toughness, becoming brittle and less shock-resistant at lower temperatures: it becomes ‘cold short’ (Stewart et al. 2000).

It is not possible to remove the phosphorous content of an ore before or during smelting; in order to avoid phosphorous enriched iron, smelters have to avoid phosphorous-rich iron ores. It is worth noting though that phosphorous can also derive in relatively large quantities from fuel ash (Schmidt 1997: 126). Phosphorous was considerably high (c. 1-2wt%) in all the samples of slag from Mwenge, whether manganese-poor or manganese-rich, excepting those from Rukomero (where phosphorous levels remained below 1wt%). The phosphoric nature of the ore from Kyakaturi, which was found to contain phosphate levels of 1.4wt%, was of particular interest. Up to a quarter of the available phosphorous in an iron ore can partition to the iron metal (Tylecote 1987: 52), which in this instance would have resulted in iron with a phosphorous content of up to 0.35wt%. This iron would likely have been strong, but brittle.

However, the limits of an acceptable phosphorous content in modern iron production (<0.04wt%) are not necessarily the same as in the past. In several documented examples, past ironworkers successfully embraced what today would be termed high-phosphorous iron (Gouthama and Balasubramaniam 2003; see also Humphris 2010 for an example from east Africa, and Ehrenreich 1985: 76-81 for a discussion of the gradual uptake of phosphoric-iron in Iron Age southern Britain). Despite the tendency towards cold-shortness, phosphorous enriched iron is “mechanically sound”, easily hot-worked and can be worked at ambient temperatures in certain conditions (Stewart et al. 2000: 276). A high phosphorous content also provides protection against corrosion, demonstrated most famously in a 1600 year-old iron pillar in Delhi (e.g. Dillmann et al. 2002).

Importantly, if the carbon content of the iron remains low, many of the negative effects attributed to high-phosphorous iron can be minimised (cf. for example, Crew and Charlton 2007: 222; see also Godfrey et al. 2003). This seems especially relevant if the carbon content of the iron is thought to rise in iron produced with a high-manganese slag. However, there are other indications that manganese may inhibit the uptake of phosphorous to the iron metal (L. Sauder pers. comm. 2013), and the positive combined effects of manganese and phosphorous have been noted experimentally (Sauder 2013). A proportion of phosphorous that has transferred to the iron will later diffuse between iron and slag inclusions during hot working, reducing the amount residual in the iron metal (Starley 1999). If manganese does act to encourage the uptake of phosphorous to the slag, the amount removed from the iron during hotworking will also presumably be increased.

As such, at the relatively low levels seen here, and depending on the intended use of the resulting iron, it is likely that the positive benefits of such a phosphorous content would be greater than any drawbacks. Furthermore, the relatively warm ambient temperatures in this part of Uganda may have reduced any perceptible effect on brittleness. Again, in the absence of analyses of iron objects from the region, this is currently impossible to confirm.

6. Conclusion

Chemical and microstructural analysis of approximately 100 samples of slag, ore and ceramic relating to bloomery iron smelting in western Uganda in the latter half of the second millennium AD, showed that the slag samples can be divided into two distinct chemical groups. One group contained slag with high levels of manganese oxide, and it is suggested that a manganese-rich mineral, known locally as entabo, was being added to the smelts at these sites. This is likely to have benefited the smelts at these sites in terms of the ease with which the iron was removed from the ore, and perhaps also in terms of the qualities of the iron that was produced. In the second group, characterised by low-manganese slag, it is likely that the manganese-rich entabo was not being added.

A deliberate addition of a separate manganese-rich material has previously been documented in the bloomery smelting of Harthorpe Mill in County Durham (Tylecote 1962: 288). Fifteenth century smelters were using nodular iron ore with a manganese content of less than 1wt%, yet contemporary slag remains contained up to 7wt% manganese oxide. This discrepancy was attributed to the addition of crushed, twelfth century slag from nearby Hoppyland. During this earlier period, smelters were using a high-manganese bog iron ore with a manganese oxide content of around 15wt%. A similar reuse of high manganese slag was seen in northwest Cameroon, where Oku smelters told of the tradition of using older slag in their smelts, which were later found to contain over 5wt% manganese oxide (Fowler 1990). These examples emphasise the benefit that adding a manganese-rich material imparts to a smelt.

In Mwenge, the coexistence of these two smelting systems in the region is intriguing. It is possible that the use of a manganese-rich flux is a later technological development that coincides with the arrival of several ironworking clans into the region during the middle of the second millennium AD. If this is the case, smelting without entabo continued to be practiced, as demonstrated at the later site of Rukomero. Many hypotheses can be put forward to explain this. The Rukomero smelters may not have been aware of the technology or how to exploit it. They may not have had access to entabo, or perhaps they chose not to use it, producing iron for a different purpose or for a different market (cf. Iles 2013). Certainly, however, smelters in Mwenge were well respected for their iron, and the goods they produced were traded across western Uganda and the wider Great Lakes region. It is possible that the high manganese contents of the ore mixes used – and the resulting slag chemistry – hold the key to their production of superior iron. The slag chemistry may prove useful once again in future provenance studies of iron objects across Uganda. Manganese-rich slag inclusions entrapped within iron objects may indicate the geographic extent of how far Mwenge iron was traded in the past (cf. Starley 1999; Paynter 2006; Blakelock et al. 2009), thus providing a measure of the regional importance of this valuable commodity from western Uganda.

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Figures

Figure 1. Regional map, showing the location of Mwenge in relation to modern towns in Uganda

Figure 2. Survey map and location of sites in Mwenge

Figure 3. Bi-plot of all slag samples in principal component space (PC1 vs. PC2)

Figure 4. BSE image of sample RKMf showing lathes of fayalite (light grey) in a glassy matrix (mid grey)

Figure 5. Photomicrograph of KTRa showing blocky fayalite (light grey), magnetitic hercynite spinels (pink, hexagonal) and the glassy matrix (dark grey). Image width $\approx 0.4\text{mm}$; PPL

Figure 6. Ternary phase diagram showing system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$, with plots for all slag samples from manganese-poor sites in terms of $(\text{Al}_2\text{O}_3+\text{TiO}_2)\text{-SiO}_2\text{-(FeO+CaO+MnO)}$ (phase diagram adapted from Slag Atlas 1995). Calculated from PED-XRF data normalised to 100%

Figure 7. Sample KRGk, showing dendritic wüstite (light grey), blocky knebelite (mid grey), cubic magnetitic-hercynite (pinkish grey) and leucitic matrix (dark grey). Black in bottom left hand corner is porosity; magnetitic-hercynite is indicated separately. Image width $\approx 1\text{mm}$; PPL

Figure 8. Photomicrograph of sample KSMk showing foils of iron (white). Image width $\approx 2\text{mm}$; PPL

Figure 9. Ternary phase diagram showing system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$, with plots for all slag samples from manganese-rich sites in terms of $(\text{Al}_2\text{O}_3+\text{TiO}_2)\text{-SiO}_2\text{-(FeO+CaO+MnO)}$ (phase diagram adapted from Slag Atlas 1995). Calculated from PED-XRF data normalised to 100%

Figure 10. Ternary phase diagram showing system FeO-MnO-SiO₂, with plots for all slag samples from manganese-rich sites in terms of (FeO+CaO+MgO+Na₂O+P₂O₅+K₂O)-MnO-(SiO₂+Al₂O₃) (phase diagram adapted from Slag Atlas 1995). Calculated from PED-XRF data normalised to 100%

Figure 11. Photomicrograph of ore sample from Kirongo showing lathes of bluish titania-rich inclusions. Image width ≈ 2mm; PPL

Figure 12. Photomicrograph of spessartine in sample of entabo; PPL

Figure 13. Hypothetical mass balance to estimate the potential maximum yield of iron from an ore with 60wt% iron oxides and 20wt% silica (Fig. 13a); from an ore with 45wt% iron oxides, 25wt% manganese oxide and 20wt% silica, resulting in knebelite with an Fe:Mn ratio of 1:1 (Fig. 13b); from an ore with 57wt% iron oxides, 13wt% manganese oxide and 20wt% silica, resulting in knebelite with an Fe:Mn ratio of 3:1 (Fig. 13c)

Tables

Table 1. Radiocarbon dates of excavated furnaces in Mwenge

Table 2. PED-XRF compositional data for all slag samples and three certified references materials, normalised to 100%. All values are the average of the three analyses of each sample. ‘Analytical total’ shows the analytical total prior to normalisation and adjustment of silica values. Values below the detection limits of the PED-XRF in all three analyses are reported as ‘/’. Values of three analyses where some are below detection limits and others are successfully measured are reported as less than or equal to the average of the successfully measured values

Table 3. PED-XRF compositional data for all ceramic and ore samples, normalised to 100%. All values are the average of the three analyses of each sample. ‘Analytical total’ shows the analytical total prior to normalisation and adjustment of silica values. Values below the detection limits of the PED-XRF in all three analyses are reported as ‘/’. Values of three analyses where some are below detection limits and others are successfully measured are reported as less than or equal to the average of the successfully measured values

Table 4. Coefficients of variation (CV) calculated from PED-XRF data of all manganese-rich and manganese-poor slag samples from Mwenge

Table 5. Correlation matrix for all slag samples from Mwenge, normalised to 100%. Correlation factors for all compounds have been arranged in a sequence that groups them according to their strongest correlations, which is likely to reflect the principal source from which these compounds are likely to have derived (i.e. ceramic, fuel ash, etc.), and colour coded in terms of the strength and direction of the correlations. Yellow shading indicates positive correlation factors over 0.6; grey shading indicates negative correlation factors over -0.6

Table 6. Correlation matrix for all manganese-poor slag samples from Mwenge. Correlation factors for all compounds have been arranged in a sequence that groups

them according to their strongest correlations, which is likely to reflect the principal source from which these compounds are likely to have derived (i.e. ceramic, fuel ash, etc.), and colour coded in terms of the strength and direction of the correlations. Yellow shading indicates positive correlation factors over 0.6; grey shading indicates negative correlation factors over -0.6

Table 7. Correlation matrix for all manganese-rich slag samples from Mwenge. Correlation factors for all compounds have been arranged in a sequence that groups them according to their strongest correlations, which is likely to reflect the principal source from which these compounds are likely to have derived (i.e. ceramic, fuel ash, etc.), and colour coded in terms of the strength and direction of the correlations. Yellow shading indicates positive correlation factors over 0.6; grey shading indicates negative correlation factors over -0.6

Table 8. EPMA compositional data for sample of entabo, unnormalised. Values below the detection limits are reported as ‘/’

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