

# Archaeo-metallurgical studies of iron smelting slags from prehistoric sites in Southern Africa

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## SYNOPSIS

The features of smelting slags from South African prehistoric sites and of related cinder material are described. Chemical analyses of twelve slag samples found in the Transvaal, Swaziland, and Botswana are reported and discussed. An attempt is made to establish a relationship between these slags and the ores collected at the Early Iron Age site of Broederstroom, which date between AD 350 and AD 600.

The liquidus temperatures of 29 slags were determined by the use of a hot-stage microscope.

The major mineral phases of 16 slags were identified by X-ray diffraction and microscopic examination. It appears that the slags investigated were formed at temperatures below 1250°C or – in some cases – at temperatures only marginally in excess of 1250°C.

## SAMEVATTING

Die eienskappe van uitsmeltslakke afkomstig van prehistoriese Suid-Afrikaanse vindplekke en verwante verkoolsels word bespreek. Die chemiese ontledings van twaalf slakmonsters wat in Transvaal, Swaziland en Botswana gevind is, word aangegee en bespreek. Daar word 'n poging aangewend om 'n verband vas te stel tussen dié slakke en ertse wat by die vindplek uit die vroeë Ystertydperk by Broederstroom, wat teruggaan na tussen 350 en 600 n.C., versamel is.

Die liquidus-temperatuur van 29 slakke is bepaal met gebruik van 'n warmplatformmikroskoop.

Die belangrikste mineraalfases van 16 slakke is deur X-straaldiffraksie en mikroskopiese ondersoek bepaal. Dit blyk dat die slakke wat ondersoek is, by temperature onder 1250°C of, in sommige gevalle, net effens hoër as 1250°C, gevorm is.

## Introduction

Much research work on the structure and constitution of pre-Roman, Roman, and medieval bloomery slags has been done in England, especially by Tylecote and his co-workers<sup>1, 2</sup> and by Morton and Wingrove<sup>3, 4</sup>. In South Africa, this aspect of archaeo-metallurgy has been studied only in the past decade, but the results of such investigations have already thrown much light on various facets of South African Iron Age technology<sup>5-8</sup>.

This paper discusses the problems, methods, and interpretations of chemical and thermal analyses and of metallographic examinations of slags, and reports the results of recent work done at the Archaeological Research Unit and at the Department of Metallurgy of the University of the Witwatersrand.

## Types of Slag and Cinder

Slag can be defined as 'dross separated in fused state in reduction of ores, vitreous smelting-refuse, clinkers' (O.E.D.). Sometimes the term *cinder* is used as a synonym for slag (O.E.D.). To avoid confusion the following definitions, proposed in a paper by Morton and Wingrove<sup>3</sup>, were adopted in a modified form for this investigation.

1. *Slag (iron-smelting slag)*. A term applied to the silicate complex formed in the bloomery process when iron ore is reduced in a smelting furnace. The main component of slag is the compound fayalite ( $\text{Fe}_2\text{SiO}_4$ ). Slag may also contain gangue minerals from the ore, impurities derived from the fuel, and in some cases wustite, silica, and various reaction products formed in the smelting process.

2. *Cinder*. Cinder is drossy solid material that collects on the top of molten slag. When removed, it resembles a mass of material infusible at the working temperature of the furnace, embedded in partially fused material. Thus cinder never reached a molten nor free-flowing condition in the furnace.

Depending on the conditions of furnace construction and the way of slag solidification either outside or inside the furnace, two classes of smelting slags can be discerned: tap slags (as in most European bloomery furnaces) and non-tap slags (as in prehistoric Southern African smelting furnaces). Two sub-types can be recognized.

Sub-type A: Flow-type slag. Solidified from molten or semi-molten condition. Lava-like rippled appearance. Black, dense, smooth surface<sup>1</sup> (Fig. 2).

Sub-type B: Furnace-bottom slag, resembling a 'flat cake'. Formed at furnace bottom, containing higher amounts of impurities from ore, fuel, and bloom. Irregular 'coral-reef' appearance (Fig. 1). Often spongy and porous. Coarser distribution of matrix and grain than in flow-type slag.

The structure of many slags is intermediate between the two sub-types described.

Besides the 'true' smelting slags, another type of slag has been described<sup>9</sup>. This type, called smithing slag, may be produced in small quantities when, under essentially oxidizing conditions, the bloom is hammered out on a smithing hearth.

The term *cinder* is also used for the fused residue produced when coal, wood, grass, or other organic materials have been burnt. Such residues, either iron free or with a low iron content, may have a superficial similarity to 'true' slag and may give rise to mis-identi-

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fications, as has happened occasionally, e.g. in the interpretation of soil found in the Mumbwa Cave in Zimbabwe, as smelting slag<sup>10</sup>. Residue cinders have also been found on old kraal sites, where dry cow-dung had caught fire<sup>11</sup> (Table II) and on the floors of grass huts that had been burnt down<sup>12, 13</sup>.

Sometimes it is difficult to classify slag-like materials found at Iron Age sites. Such 'abnormal' slags have been reported from several Magaliesberg sites, especially from the large Middle Iron Age site Olifantspoort<sup>5</sup>. The

analysis of these slags shows very high silicon contents, low iron contents, and high alkalinity (Table II). No convincing explanation for the formation of these slags has so far been given. The iron contents appear to be too low for 'true' smelting slags, but too high for cinder originating from burnt organic material. One could speculate that the high silicon content in the slag was caused by a corresponding high silicon content in the mother-ore, or by the addition of sand or crushed quartzite as flux, or by the absorption of silicon from a grass bed at the furnace bottom. It has also been suggested that iron slags of low iron content could have been derived from copper-iron pyrites<sup>5, 14</sup>, or that such slags are the result of re-smelting or smithing procedures.

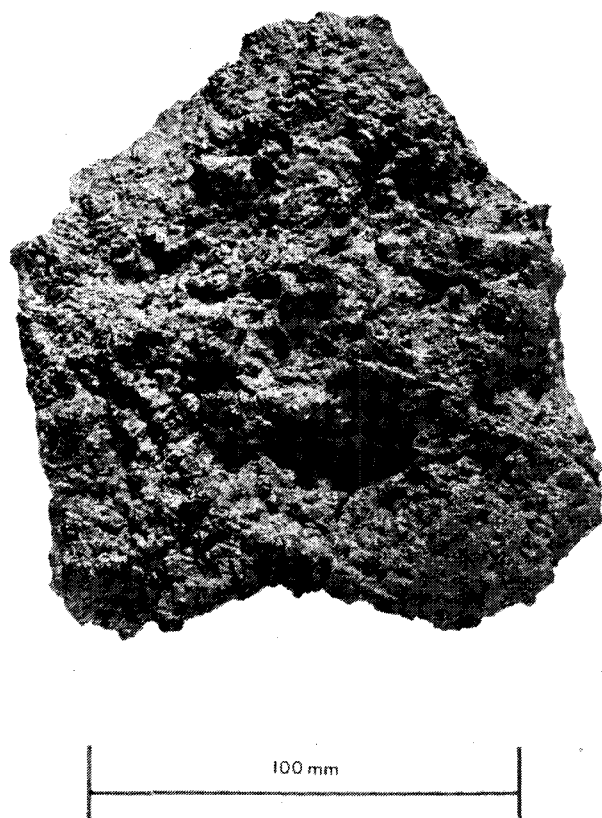
The only conclusion one can draw from the analysis of such 'pseudo-smelting slags', 'slag-like cinders', and other abnormal smelting products is that a slag should be regarded as evidence for Iron Age smelting operations only when it is found in a satisfactory context (with furnace debris, tuyère fragments, or ore and metal pieces), and when its analysis falls into the ranges established for 'normal' Iron Age smelting slags (Table II).

### Chemical Analyses of Slags

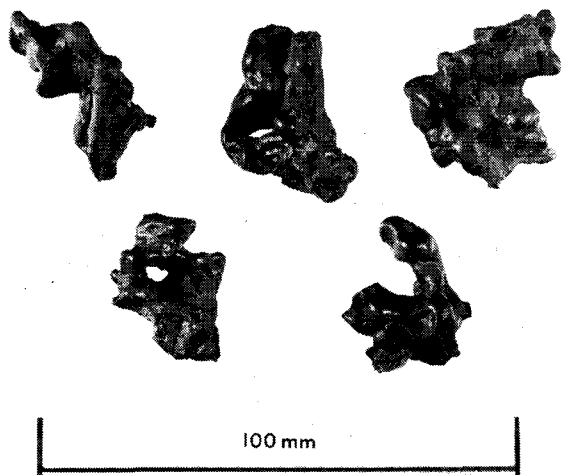
The value, the problems, and the limitations of chemical analyses of slags are evident from Table I. The table shows a general uniformity for slag composition over a very wide area and over very long periods, but also considerable differences between samples taken from the same site (e.g. samples 1 and 2). These analyses support the concept of a single basic smelting technology in South Africa. Apparent regional differences may be due more to the variable character of the raw materials than to different production methods. Differences in the analysis of slags collected at the same furnace site can be ascribed mainly to the non-standardized production methods of the Iron Age smelters.

Tables I and II show that the iron contents for 15 samples from the central and western Transvaal, Swaziland, and Botswana (Fig. 3) are in a fairly close range (from 43 to 54 per cent iron), but that the proportions of ferric to ferrous iron vary in these samples. The calculated  $\text{Fe}_2\text{O}_3$  contents are somewhat lower in the Later Iron Age samples (average 11,5 per cent) than in the Early Iron Age samples (average 16,7 per cent), an observation that could point to a better reduction efficiency acquired by long experience. However, not too much importance should be placed on such calculations, since the sampling pattern may often have been erratic and very old slags may have been oxidized by soil reactions and weathering<sup>3</sup>.

The alkalinity of the samples from 18 different sites varies considerably (Table II). The slags from the eastern and northern Transvaal differ in this respect from those found in the western and central Transvaal. Especially interesting are the high lime values in the samples from Vendaland and the Phalaborwa area (samples 10 to 12, Table I, Table II). Two explanations offer themselves: either the Venda and Phalaborwa smelters used lime-containing flux, or the slags absorbed lime from the charcoal fuel. The ashes of some bushveld trees (e.g. leadwood and mopane) burnt for charcoal are known for their high



**Fig. 1—A furnace bottom slag (original mass 1035 g) found 20 cm below the present surface at the Broederstroom Early Iron Age site (age 5th century AD)**



**Fig. 2—A flow-type slag found at Broederstroom Early Iron Age site**

TABLE I  
ANALYSES OF SLAG SAMPLES FROM SOUTH AFRICA, SWAZILAND, AND BOTSWANA

Sample no.	1	2	3	4	5	6	7	8	9	9	11	12
Investigator	A.R.U. (Wits)	A.R.U. (Wits)	A.R.U. (Wits)	A.R.U. (Wits)	A.R.U. (Wits)	Küsel	A.R.U. (Wits)	A.R.U. (Wits)	A.R.U. (Wits)	A.R.U. (Wits)	Küsel	v.d. Merwe & Killick
Access no. sample no.	24/73	24/73	24/73	7/63	28/64		23/80	37/80	39/73	27/73		PQ1-Mb
Site	Broeder- stroom	Broeder- stroom	Broeder- stroom	Melville Koppies Nat. Res	Melville Koppies Nat. Res	Farm Modder- fontein Groot Marico Distr.	Farm Schiet- kraal Zeerust Distr.	Lobatsi Estate	Farm Caldwell Mbabane Distr.	Farm Schuins- hoogte Levubu Distr.	Farm Schield Sibasa	Farm Square Phla- borwa Distr.
Area or district	Pretoria	Pretoria	Pretoria	Jhb.	Jhb.	W. Tvl.	W. Tvl.	Botswana	Swaziland	Venda	Venda	E. Tvl.
Sample taken at	K Flow pattern slag 5th c AD	K Cake pattern slag 5th c AD	X	Upper furnace base 11th c AD	Lower furnace 22 cm below rim 18/19th c AD		Furnace No. 1 50 cm B.P.S.		Furnace site	Surface sample furnace site		
C <sub>14</sub> age of site												
Constituent	Expressed as	%	%	%	%	%	%	%	%	%	%	%
Silicon	SiO <sub>2</sub>	20,2	24,1	25,28	21,76	16,9	19,6	32,5	21,93	2,73	23,7	20,25
Aluminium	Al <sub>2</sub> O <sub>3</sub>	3,24	4,72	6,94	5,16	7,7	5,8	2,0	11,48	9,5	5,0	4,28
	Total	77,4	69,7	13,38	11,64	67,77	72,4	67,6	10,54	46,5	60,62	6,83
Ferrie iron	Fe <sub>2</sub> O <sub>3</sub>	60,4	57,7	44,66	56,28	—	—	—	44,79	—	—	43,40
Ferrous iron	FeO	0,34	0,58	0,96	0,52	0,75	0,97	0,38	1,49	2,14	2,0	3,60
Magnesium	MgO	0,60	1,16	1,92	1,47	0,21	1,81	0,42	3,93	5,98	8,20	12,33
Calcium	CaO	0,57	0,55	0,32	0,39	0,20	0,10	0,10	0,36	0,32	0,46	0,44
Sodium	Na <sub>2</sub> O	0,11	0,24	0,79	0,77	0,69	1,21	1,09	1,68	8,22	2,4	1,45
Potassium	K <sub>2</sub> O	0,21	0,33	0,38	0,31	0,50	0,23	0,11	0,41	1,84	2,30	4,68
Titanium	TiO <sub>2</sub>	0,21	0,28	0,03	0,00	0,48	0,31	0,11	0,31	1,86	2,23	0,58
Phosphorus	P <sub>2</sub> O <sub>5</sub>	<0,01	<0,01	<0,01	0,00	—	0,06	0,04	0,12	0,05	—	0,01
Chromium	Cr <sub>2</sub> O <sub>3</sub>	0,11	0,25	3,55	0,13	4,27	3,28	2,48	1,94	0,59	0,7	0,26
Manganese	Mn <sub>2</sub> O <sub>4</sub>	—	—	1,79	1,34	—	—	—	0,1	—	—	—
Loss on ign.	H <sub>2</sub> O, CO <sub>2</sub>	—	—	—	—	—	—	—	—	—	—	—
Total iron	Fe	54,18	48,79	44,07	51,89	47,4	50,78	47,27	42,19	32,52	42,4	38,5
(calculated)												
Analyst	Analytical Mintek AD 187/2	Chemistry Mintek AD 187/3	Division* Mintek AD 187/1	Mintek AA972/9	Mintek AA972/9	Steyn	Mintek AD 90/2	Mintek AD 90/3	Mintek AA991/1	Mintek AD90/1	Steyn	
Ref. no.	—	—	—	6	6	7	—	—	—	—	7	8

\* Methods of analysis: X-ray fluorescence, atomic-absorption spectrophotometry (Na<sub>2</sub>O), volumetric analysis (FeO).

A.R.U. = Archaeological Research Unit

Wits = University of the Witwatersrand, Johannesburg

Mintek = Council for Mineral Technology (formerly the National Institute for Metallurgy)

lime contents<sup>8,15</sup>, and this may well account for the high lime content in some slags. One sample taken from a furnace at Levubu (Table I, sample 10) showed also an extraordinarily high potassium content (8,2 per cent K<sub>2</sub>O). No satisfactory explanation can be given for this feature, but perhaps a charcoal fuel with a very high potassium content was used, intentionally or unintentionally, in the smelting process.

### Composition as a Guide to Provenance

The relationship between the chemical compositions in a set of slags and of ores can serve as a guide to the provenance of a particular ore used at a smelting site. Especially indicative for this purpose is the presence and percentage of certain minor and trace elements (e.g. manganese, titanium, vanadium, cobalt, nickel) in both ore and slag. Sometimes the quantities of such indicator elements are compared directly, but often couples or groups of elements are used for the calculation of correlation factors.

In South Africa, where many iron ores are titaniferous, the titanium contents as well as the proportions of titanium to other elements have been used to trace the provenance of slags from particular ore sources.

An instructive study on the provenance of slags has been made by Van der Merwe and Killick<sup>8</sup>, who compared the analyses (ratios) of a number of slags found at the 'Square' smelting site (25 km south-east of Phalaborwa) with analyses of various slag and ore samples from other places in the Phalaborwa-Gravelotte area. The results of this study using Fe/Ti ratios as well as Ti/Ca ratios for the comparison of slag groups suggest that the ores used at 'Square' came from an orebody some 20 km to the east of the smelting site.

At the Archaeological Research Unit the analyses for a number of slags and ores from the Broederstroom fifth century Iron Age site<sup>5, 8, 16, 17</sup> were used to calculate Mn/Ti ratios for these samples and to match them in pairs (Table III). The Mn/Ti ratios were preferred to the

Fe/Ti ratios, since only part of the iron in the ore used for smelting may find its way into the slag, while the remainder of the iron in the ore is reduced to elemental iron. Because of non-equilibrium conditions, the partitioning of the iron between the various phases of the smelting process is not predictable. It is therefore preferable to use some element other than iron in such studies, especially manganese since, as Tylecote<sup>1</sup> and Todd<sup>18</sup> have pointed out, manganese in ores smelted by the bloomery method reports almost exclusively to the slag.

Table III gives the Mn/Ti ratios for five ores and seven slags found at the Broederstroom site. A relationship is evident between ore samples taken at position S.W. Donga exposure (Mn/Ti ratios 0,65 and 0,69) and a slag sample collected at position K (flow) (Mn/Ti ratio 0,62).

Three samples of ore collected at positions K, Azv, and Y (Table III) are in a sufficiently close group to have come from a single (not located) source supplying ore for the slags found at position 16 and K. Similarly, ore from position Bu and slag from position L(TI) may be related. For the other slags, no correlations with an ore could be established.

It appears that ores taken from the S.W. Donga exposure were used at smelting sites about 600 m away. Other ores may have been taken from shallow surface occurrences or may have been brought from iron deposits further away, e.g. from a known rich ore deposit on the farm Welgegund<sup>16</sup> adjoining the Broederstroom site. No samples from these ore occurrences were available for testing.

### Problems in the Interpretation of the Analyses

The principles and methods used in the sampling of materials in mining and industrial practice should also be applied during the sampling of archaeo-metallurgical materials (ores, slags, and metal objects). In addition, some particular problems should be considered.

Since the number of specimens found at smelting sites

TABLE II  
RANGE OF VALUE FOR SLAGS FROM IRON AGE SITES IN THE TRANSSAAL, SWAZILAND, AND BOTSWANA AND FOR A CINDER SLAG FROM BOTSWANA

Constituent	Expressed as	Range for 9 samples from Broderestroom site 24/73	Range for 6 samples from central and western Tvl. Swaziland, and Botswana	Range for 3 samples from northern and eastern Transvaal	Range for 7 samples from Olifantspoort	Cinder slag from a Botswana site
Silicon	SiO <sub>2</sub>	20 - 29,2	16,9 - 32,5	20,3 - 32,3	62,6 - 69,3	66
Aluminium	Al <sub>2</sub> O <sub>3</sub>	3,2 - 5,9	2,0 - 11,5	4,3 - 9,5	10,4 - 17,0	2,6
Iron	Fe	43,1 - 54,2	42,2 - 51,9	32,5 - 42,4	5,3 - 8,0	0,63
Magnesium	MgO	0,1 - 1,5	0,4 - 1,5	2,0 - 3,6	1,3 - 4,4	3,6
Calcium	CaO	0,6 - 1,4	0,2 - 3,9	6,0 - 12,3	1,3 - 2,4	7,8
Sodium	Na <sub>2</sub> O	0,03 - 0,57	0,1 - 0,4	0,3 - 0,5	0,1 - 0,3	0,7
Potassium	K <sub>2</sub> O	0,1 - 0,5	0,6 - 1,7	1,5 - 8,2	2,4 - 3,5	9,4
Titanium	TiO <sub>2</sub>	0,2 - 0,5	0,1 - 0,5	1,8 - 4,7	0,7 - 1,0	0,25
Phosphorus	P <sub>2</sub> O <sub>5</sub>	0,1 - 1,1	0,1 - 0,5	0,6 - 2,2	0,1 - 0,6	3,3
Chromium	Cr <sub>2</sub> O <sub>3</sub>	< 0,05	< 0,01 - 0,1	0,01 - 0,05	0,1 - 0,3	
Manganese	Mn <sub>2</sub> O <sub>4</sub>	0,06 - 1,56	0,1 - 4,3	0,3 - 0,7	0,12 - 0,22	0,13
Reference		Table I (nos. 1-3) and Table II of ref. 5 (nos. 13-17 and no. 32)	Table I (nos. 4-9)	Table I (nos. 10-12)	Table II of ref. 5 (nos. 30-26)	Ref. 11

**TABLE III**  
CORRELATION RATIOS OF ORES AND SLAGS FOUND AT BROEDERSTROOM SITE 24/73

Sample	Position code of sample	% Manganese	% Titanium	Ratio Mn/Ti	Reference for position
Ore	K	0,065	0,204	0,34	Ref 16 - Table I, no. 2
Ore	Azv	0,077	0,210	0,36	Ref 16 - Table I, no. 4
Ore	Y	0,054	0,126	0,43	Ref 16 - Table I, no. 5
Ore	S.W. Donga exposure sample a	0,124	0,192	0,65	Ref 16 - Table I, no. 1
Ore	S.W. Donga exposure, sample b	0,07	0,102	0,69	Ref 6 - Table I, no. 2
Ore	Bu	0,108	0,078	1,39	Ref 16 - Table I, no. 3
Slag	16	0,043	0,121	0,36	Ref 5 - Table II, no. 13
Slag	K	0,065	0,144	0,45	Ref 5 - Table II, no. 32
Slag	K (flow type)	0,078	0,126	0,62	Present paper - Table I, no. 1
Slag	X	0,178	0,198	0,9	Present paper - Table I, no. 3
Slag	L (TI)	0,209	0,132	1,58	Ref 5 - Table II, no. 16
Slag	K (cake type)	0,547	0,282	1,94	Present paper - Table I, no. 2
Slag	L (T2)	0,749	0,132	5,67	Ref 5 - Table II, no. 17

is often limited, a collection of ores and slags may be the result of random sampling only. Variations in temperature, fuel/ore ratio, volume of air blown, and other operational factors would have created fluctuating conditions in the smelting furnaces and would have influenced the results of even a single smelt. Especially suspicious is a collection of slag samples out of context with a particular smelting furnace, e.g. from excavated smelting sites. Such a collection may represent a mixture of slags produced under different conditions or from different periods. Only material from a single slag specimen should be analysed — mixed samples should be avoided. Slags may also contain various admixtures of charcoal and ore particles, of scrap iron, and of rejected smelter's bloom. Ore pieces found near furnaces may have come from deposits worked out or unknown now, or they may represent treated or enriched ore material. Soil conditions, leaching, and weathering may have changed the composition of the ore and slag samples<sup>19</sup>. Finally, the methods used for testing may have a bearing on the analytical results, especially if the constituents are present in small amounts as in the case of trace and minor elements.

To overcome such problems inherent in the study of prehistoric metal production, statistically valid sampling procedures involving very large numbers of samples have been used in some American, German, and Russian archaeo-metallurgical research work. In a single project that tried to find the ore sources for European metal production during the Bronze Age, over 9000 specimens were analysed<sup>20</sup>. Such large-scale projects are hardly feasible under South African conditions. In past decades, probably fewer than one hundred analyses of iron slags and iron artefacts collected at Southern African sites have been published. However, most of these analyses fall into reasonably close ranges of elemental composition and may give, if carefully interpreted, results useful for the evaluation of Iron Age metallurgy in Southern Africa.

#### Determination of Liquidus Temperatures

The equipment used in the tests on the thermal characteristics of smelting slags was designed and built by Mintek (then the National Institute for Metallurgy).

The construction and operational details are given elsewhere<sup>21,22</sup>. Here it is sufficient to mention that Pt6Rh-Pt30Rh wires were used for the thermocouples which, by the basic principle of the hot-stage microscope technique, acted as both heating and measuring elements, alternately changing role in each half cycle of the current. Thus, in a conventional 60-cycle system, each period lasted exactly one-sixtieth of a second, and the rate of cooling between two heating cycles was negligible even at temperatures over 1600°C.

Only a few milligrams of the powdered representative sample was subjected to testing; the powder was contained between the two thermocouple legs under the junction point.

The heating was fast enough to reach 900 to 950°C within a minute. At above 1000°C the automatic heating-rate control was switched on, the rate being set at 10 or 20°C per minute. This permitted sufficient soaking time, which was critical for the detection of the low-temperature sintering of the sample and the melting of the primary phase.

The e.m.f. generated by the thermocouple was measured by use of either a standard Cambridge potentiometer or a TR 8355 Mini-Multimeter.

#### Accuracy of the Measurements

By the very nature of the mode used for the observation of the melting point, the applied form of hot-stage microscope technique is suitable primarily for measurements carried out on pure white or slightly greyish slags. In this case, in a molten, transparent thin layer of slag, the disappearance of residual floating crystals representing the last solid, high-melting phase could clearly be observed when the temperature was increased slowly. However, the majority of industrial and pre-industrial slags obtained in conventional smelting operations are dark grey, often pitch-black when cold. Even if completely molten, the thin layer of slag pool on the thermocouple remains entirely opaque. As a consequence, the melting of the last phase may not be clearly evident and may result either in low readings or in readings that are higher than the actual melting temperature. Fortunately, the difference is within a reasonable range as comparisons between the melting points of synthetic white slags

and dark plant slags of identical composition indicated. A large number of tests were conducted in this way. In certain cases the actual melting point of the tertiary phases may be higher than that read from the instrument; that is, only partial melting of the material was recorded. On the other hand, once considerable experience has been gained in this technique, the accuracy of the determinations and the reproducibility of the readings is good. For example, with light-coloured slags the accuracy is within the range of 3 to 5°C around 1450 to 1500°C; with dark slags it is 10 to 15°C.

As a correlation test, one slag sample (no. 8, Table IV) was also tested by the National Building Research Institute, where different types of equipment (Leitz heating microscope and a Du Pont differential thermal analysis cell) were used for the determination of the thermal phases. The results of these tests are given in Table IV for sample 29. The initial sintering temperatures for sample 29 were found to be lower than those recorded for the same slag (sample 8, Table IV), but for phase 3 the results of the temperature measurements

obtained in the two laboratories show relatively little difference (5 to 8 per cent).

Pertinent to their behaviour during heating on the thermocouple as observed under the microscope, most of the materials seem to go through a three-phase melting process. In the first phase, either simple sintering or actual melting occurs as indicated by the volume decrease or actual liquation (melting) of various amounts of the samples. After the completion of this process, the physical conditions of the material seem to remain unchanged with further increase in temperature, until a well-defined temperature is reached, when new melting becomes evident. In other cases, this particular phase is characterized by partial melting; thus a continuous change in the consistency of the solids can be observed, which prevails up to a point, when, again at a well-defined temperature, the sample becomes completely molten. Table IV shows these melting phases. The column 'Initial sintering' also involves the start of the melting of the primary phase. The melting manifests itself in the visible movement of the solids on the thermo-

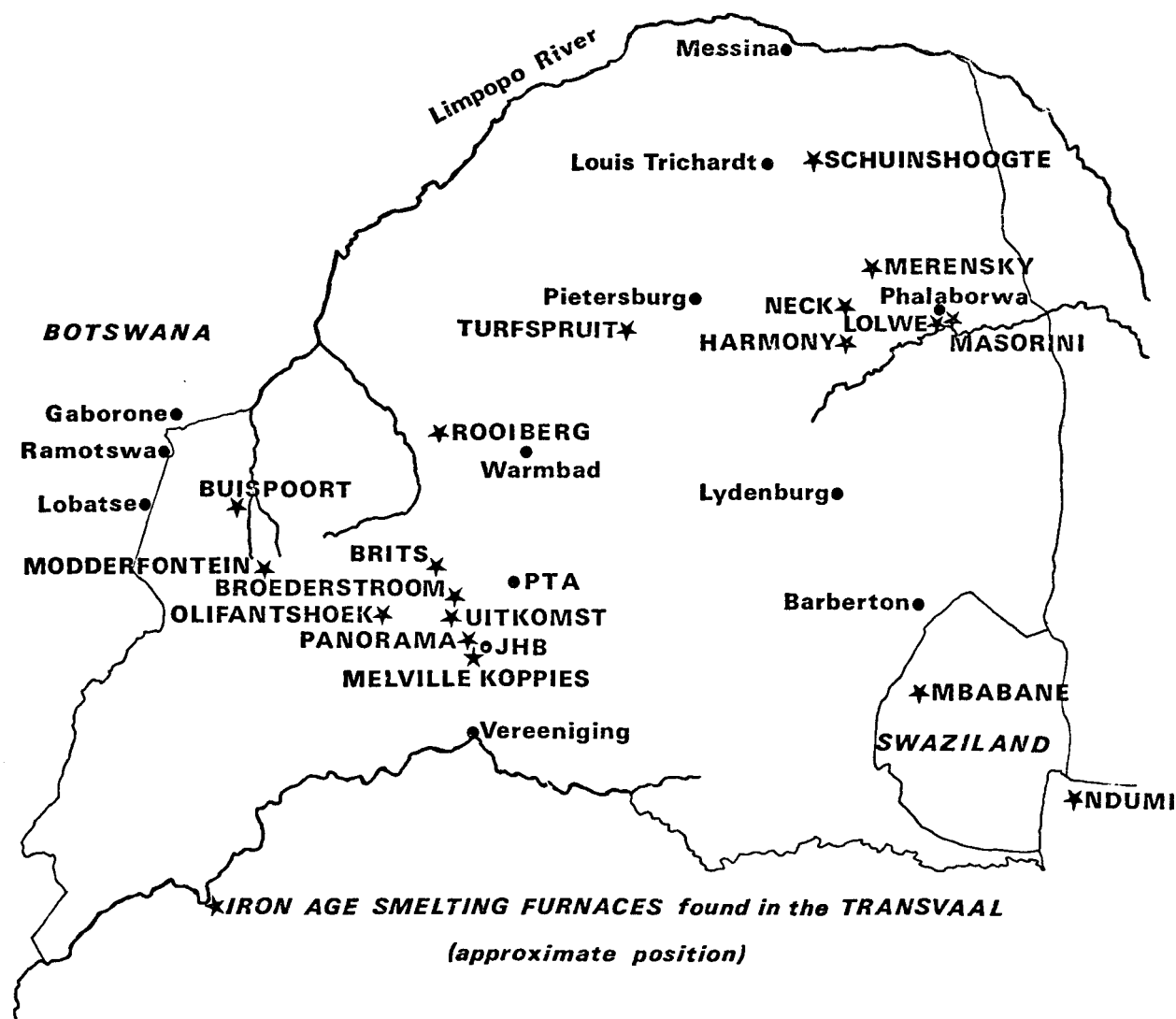


Fig. 3—Map showing the location of Iron Age smelting sites in the Transvaal, Botswana, and Swaziland

TABLE IV  
THERMAL CHARACTERISTICS OF FURNACE SLAGS

Sample no.	Site	Cat. no.	Position	Notes	Initial sintering, °C	Intermediate phases, °C, or continuous transition	Fully molten final phase °C (flow)	Notes	Ref.
1	Broederstroom	24/73K		Sample from slagged tuyère	1460/1465		1537		
2	Broederstroom	24/73 K	FGH 2,50-3,50		1380		1474		
3	Broederstroom	24/73 K		Core of slag sample. Det. in Argon.		1342	1445	) 2 det. on same sample	
4	Broederstroom	24/72 K		Core of slag sample. Det. in argon. Repeat det. of sample 3.			1455/1462		
5	Broederstroom	24/73 K		Non-magnetic slag sample	1280/1290	Distinct liquid second phase 1420/1450	1530		
6	Broederstroom	24/73 K		Magnetic slag sample	1270/1275	Distinct liquid second phase 1385/1390	1470/1480		
7	Broederstroom	24/73 K		Flow patterned slag	1390	Distinct bulk phase 1455/1460	1504/1508		
8	Broederstroom	24/73 K		Furnace bottom cake	(a) 1340/1380	(b) 1420	(a) 1450/1455 (b) 1451/1455	2 det. on same sample but det. on different places of sample	
9	Broederstroom	24/73 X		Sample I	1370	Cont. transition	1452		
10	Broederstroom	24/73 X		Sample II	1410	1460/1462	1475		
11	Broederstroom	24/73	West side 22	Slag sample from slagged tuyère	1390		1460/1465		
12	Melville Koppies	7/63		Upper furnace		1535	n.d.	Refractory material, slight fusion	
13	Melville Koppies	7/63		20 cm B.P.S. upper furnace	1100	1290	1445		
14	Melville Koppies	7/63		30 cm B.P.S. upper furnace	1362		1480		
15	Melville Koppies	28/64		Inside lower furnace			1444		
16	Olifantspoort	20/71	Hut/floor B	Near furnace A		1423	1512		
17	Olifantspoort	20/71		Surface slag	1383		1420		
18	Olifantshoek	56/73			1150/1200		1430		
19	Farm Modderfontein Groot Mario				1030 deform.	1500 hemisph.	1520 flow		Kusel Steyn Ref 7
20	Farm Schietkraal near Zeerust	23/80	Furnace I	50 cm B.P.S.	1350	Cont. transition	1472/1490		
21	Farm Schietkraal near Zeerust	23/80	Furnace III	10 cm B.P.S.	1375/1385		1480/1485		
22	Farm Schietkraal near Zeerust	23/80	Furnace IV		1265		1385. At 1420: All phases liquid-complete fusion		
23	Lobatsi Estate Botswana	37/80			1315/1318		n.d.	Refractory material, high Al and Ca content	
24	Farm Caldwell near Mbabane (Swaziland)	39/73		Tuyère slag			1485		
25	Lulukop Phalaborwa				1310 deform.	1550 hemisph.	Not molten	) Kusel Steyn	
26	Farm Schield Sibasa (Vendaland)				1180 deform.	1210 hemisph.	—	) Ref 7	
27	Farm Schuynshoogte Levubu (Vendaland)	27/73			1225/1257		1350	)	
28	Laboratory Experiment 26 in reconstructed furnace				1430		1491 in air 1495 in argon		Ref 6, p. 238
29	Broederstroom	24/73 K		Furnace bottom cake			(a) 1460	Apparatus used for det. (a) Leitz heating microscope (b) Du Pont differential thermal analysis cell, made at National Bldg Research Inst., Pretoria	
				(sample taken from same specimen as used for determ. no. 8)	(b) 1270		(b) 1440		

couple wire, and it is brought about by the collapse of the primary phase. As will be obvious from the table, the temperature range of this phase is rather wide, extending from 1100 to 1380°C. In samples 5, 6, 13, 22, 27, and 29, it corresponds by-and-large to the disappearance of the fayalite phase. In most of the other samples, judged solely by their melting behaviour in the hot-stage microscope, the low-melting fayalite would appear to be altogether absent. However, X-ray-diffraction studies indicated that, in the majority of the slags, fayalite is the low-melting temperature phase.

The intermediate phases, whatever their composition, also represent a wide temperature range. Where high-melting intermediate phases (higher than 1500°C) were recorded (slags 12, 19, and 25), the slags are of a somewhat dubious nature and could hardly be regarded as true slags representing the operation of ancient primitive furnaces.

The bulk of the samples submitted to temperature measurement have a final melting point in the range 1420 to 1480°C. The excessively high-melting specimens with melting points of 1504 to 1550°C may be the products of weathering processes or of slags that contain foreign matter such as furnace walls, tuyère materials, etc. Consequently, it is rather questionable whether any of these 'slags' reached a final molten state in the course of the smelting operation in furnaces of the South African Iron Age.

### Phase Diagrams

The high FeO-SiO<sub>2</sub> system in its primary melting phase can probably be represented reasonably well by the quasi-ternary SiO<sub>2</sub>-FeO-anorthite phase diagram of Lewin *et al.*<sup>23</sup>. The two predominant compounds in the slag systems are FeO and SiO<sub>2</sub>, or in the primary melting phase wustite and fayalite, both of them distinct with low melting points when taken separately. One would thus expect slags of low melting point, generally below 1350°C.

Morton and Wingrove<sup>3, 4</sup> have described a method for the calculation of the constitution and thermal characteristics of smelting slags from a quasi-ternary phase diagram constructed in terms of SiO<sub>2</sub>, FeO (including FeO equivalents of Fe<sub>2</sub>O<sub>3</sub> and MnO), and anorthite (CaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>). It is not certain whether this method is applicable to South African non-tap slags, which solidify at the furnace bottom and are less homogeneous than tap slags, which are discharged as viscous free-flowing matter from the smelting furnace into a pit or a channel outside the furnace.

However, an attempt was made to calculate the mineralogical constitution of three slags from the Broederstroom site—24/73K (flow), 24/73K (cake), and 24/73X—from the analyses of these slags (Table I, 1 to 3) and from plotting the calculated percentages of the components SiO<sub>2</sub>, FeO, and anorthite on the phase diagram as proposed by Morton and Wingrove<sup>3, 4</sup>. These slags concentrate in the region of low melting point (fayalite) of the diagram, which corresponds to melting temperatures of about 1150 to 1200°C.

The actual melting (flow) temperatures determined by thermal analysis (i.e., by hot-stage microscope and

differential thermal analysis, Table IV) in the range 1420 to 1480°C are much higher than those calculated from phase diagrams. This could be due to various reasons. For example, even in the simple FeO-SiO<sub>2</sub> binary-phase diagram, a very sharp increase in the melting point would occur with a decrease of the fayalite content. Furthermore, the increased temperatures of the secondary, and especially of the tertiary, melting phases may be due to subsequent reactions between the primary fayalite or wustite and the oxides present in the slag.

FeO could be incorporated in the slag system in the form of iron gehlenite (Ca<sub>2</sub>FeSiAlO<sub>7</sub>), as a quaternary CaO-MgO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> compound<sup>23</sup>, as kirschsteinite (CaO, FeO, 2SiO<sub>2</sub>), or as similar compounds<sup>4</sup>. FeO could also combine with available Al<sub>2</sub>O<sub>3</sub> to form the spinel hercynite, and the slag area could then move in the higher-temperature hercynite phase.

Furthermore, such a quasi-ternary phase diagram assumes that, besides the three phases of the FeO-SiO<sub>2</sub>-anorthite system, no other components are present in significant amounts in the slags investigated. This is an ideal condition and is rarely achieved in practice. In slag samples from Southern African sites, constituents such as magnesium, manganese, titanium, potassium, and phosphorus are often found in considerable amounts, as can be seen from the analyses recorded in Table I. Compounds formed by these and other slag constituents (e.g. various aluminium silicates, plagioclase, and spinels like hercynite and ulvite as observed by Steyn<sup>7</sup>) may well affect the validity of phase diagrams designed as a three-component system.

### Role of Experimental Work

Valuable information on the significance of the results from investigations of metallurgical slags could be obtained from iron-smelting experiments in re-constructed well-instrumented Iron Age furnaces. In such furnaces, the temperatures during smelting and cooling periods could be observed. The slags produced could be analysed, and correlations between the flow temperatures of slags and operational furnace temperatures could be established.

Little work on such lines has been done in South Africa. Slag 28 (Table IV) was produced in a smelting experiment at the Archaeological Research Unit, but the operational temperature in the furnace was measured at only one control point (near the tuyère end). It is intended to continue such experiments at extended temperature ranges when the resources for such a project become available.

### Microscopic and X-ray-diffraction Examinations

Some of the slag samples consisted of particles of a weak spongy substance and tended to decrepitate, while others consisted of much denser material. The dense slag particles had rounded edges and a smooth but irregular surface, as can be seen from Fig. 2. The appearance of these particles indicated that the temperature reached was high enough to cause softening and plastic flow of the material.

Fragments of a tuyère that were examined (sample 1, Table IV) showed that reactions took place between



the tuyère material and the charge. These reactions resulted in the formation of a black layer of material on the inner surface of the tuyère, but the outer layers of the tuyère were not affected. The fragments originated from the tip of the tuyère, where the temperature must have been at or near its maximum<sup>24</sup>.

Representative samples of various slags were pulverized and analysed by X-ray diffraction. The major phases identified are shown in Table V in order of decreasing abundance. As can be seen, most of the slags showed distinct similarities, only slag 27 being distinctly different from the rest. The slags consisted mainly of iron and silicon oxides in varying proportions.

The major phases were positively identified in all the slag samples except in slag 27, in which one or more of the major phases were not identified.

TABLE V

MAJOR MINERALOGICAL PHASES IN SLAG SAMPLES (X-RAY DIFFRACTION ANALYSIS)

Sample no. *	Site and catalogue no.	Phases
1	Broederstroom 24/73K	$\alpha$ -SiO <sub>2</sub> , low $\alpha$ -cristobalite
2	Broederstroom 24/73K	Fe <sub>2</sub> SiO <sub>4</sub> , FeO, $\alpha$ -SiO <sub>2</sub>
7	Broederstroom 24/73K	
8	Flow	FeO, Fe <sub>2</sub> SiO <sub>4</sub>
8	Broederstroom 24/73K	
	Cake	Fe <sub>2</sub> SiO <sub>4</sub>
9	Broederstroom 24/73X	Fe <sub>2</sub> SiO <sub>4</sub> , FeO
12	Melville Koppies 7/63	Fe <sub>2</sub> SiO <sub>4</sub> , $\alpha$ -SiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub>
		FeO
13	Melville Koppies	
	7/63 - 20 cm BPS	Fe <sub>2</sub> SiO <sub>4</sub> , $\alpha$ -SiO <sub>2</sub>
14A	Melville Koppies 7/63	$\alpha$ -SiO <sub>2</sub>
14B	30 cm BPS	$\alpha$ -SiO <sub>2</sub> , low $\alpha$ -cristobalite
15	Melville Koppies 28/64	Fe <sub>2</sub> SiO <sub>4</sub> , FeO, $\alpha$ -SiO <sub>2</sub>
16	Olifantspoort 20/71B	$\alpha$ -SiO <sub>2</sub>
17	Olifantspoort 20/71	$\alpha$ -SiO <sub>2</sub> , low $\alpha$ -cristobalite
18	Olifantshoek 56/73	Fe <sub>2</sub> SiO <sub>4</sub> , $\alpha$ -SiO <sub>2</sub>
24	Mbabane 39/73	Fe <sub>2</sub> SiO <sub>4</sub> , FeO
27	Schuinshoogte 27/73	FeO
28A	Lab Exp No. 26	Fe <sub>2</sub> SiO <sub>4</sub> , $\alpha$ -SiO <sub>2</sub> , FeO
28B	Lab Exp No. 26	Fe <sub>2</sub> SiO <sub>4</sub> , FeO, $\alpha$ -SiO <sub>2</sub>

The microscopic examination of suitable slag samples showed the mode of occurrence of the different phases. The appearance of slag 15 is evident from Fig. 4. The structure consists mainly of dendrites of wustite in a slag matrix. The amount of metal in the slags examined was very small, while the amount of unreduced wustite varied widely from one sample to the next.

The slags prepared in the laboratory (samples 28A and 28B) had a structure similar to that of the archaeological samples, as can be seen in Fig. 5, which shows dendrites and grains of wustite in a fayalite matrix.

The presence of  $\alpha$ -SiO<sub>2</sub> as the only form of free silica in several of the slags examined shows clearly that the furnace temperature attained by these slags could not have been greater than 1250°C. It is well known<sup>24</sup> that  $\alpha$ -SiO<sub>2</sub> is transformed to tridymite at 870°C, or to cristobalite at 1250°C. The reverse transformations do not occur during cooling. Thus, samples containing  $\alpha$ -SiO<sub>2</sub> and no tridymite or cristobalite underwent temperatures lower than 1250°C. It can be seen from Table V that more than half the samples examined were subjected to temperatures below 1250°C.

The presence of  $\alpha$ -SiO<sub>2</sub> and low  $\alpha$ -cristobalite in samples 1, 14B, and 17 shows that the temperature must have exceeded 1250°C for these samples. The low proportion of cristobalite suggests that either the temperature was only marginally in excess of 1250°C or that the time for which the quartz was exposed to this temperature was very brief. The former would appear to be the case since the production of sponge iron was a lengthy process<sup>25</sup>. (The transformation of quartz to tridymite and cristobalite is determined by temperature and time since it occurs by the breaking and reforming of bonds. Thus, if the reaction sequence is quartz→tridymite→cristobalite, it is unlikely that a sample will contain only quartz and cristobalite but no tridymite. Therefore, it can be concluded that the transformation was direct from quartz to cristobalite.)

The phases in slag 1 are of fundamental importance

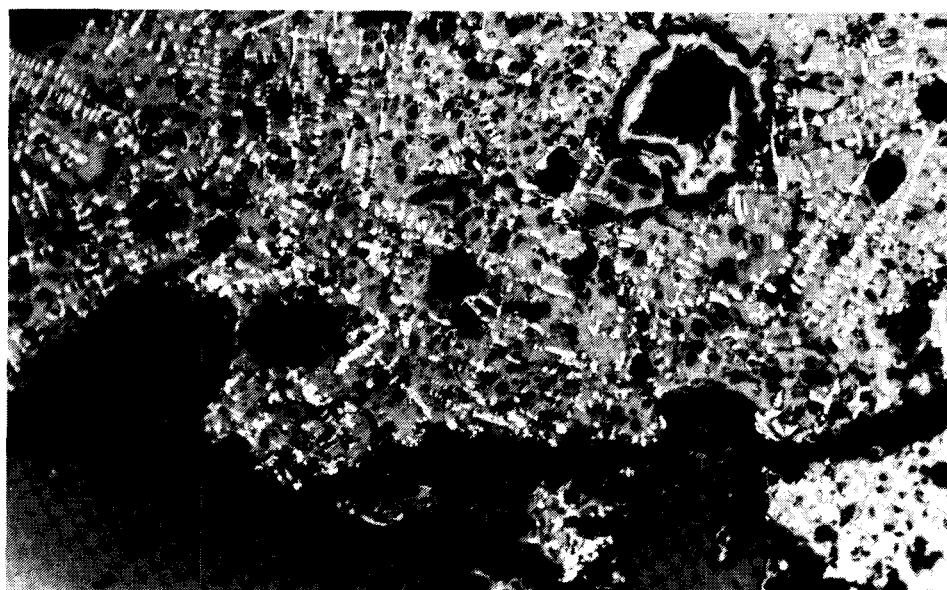


Fig. 4—A typical slag microstructure showing wustite dendrites in a matrix of fayalite (polished, 120x)

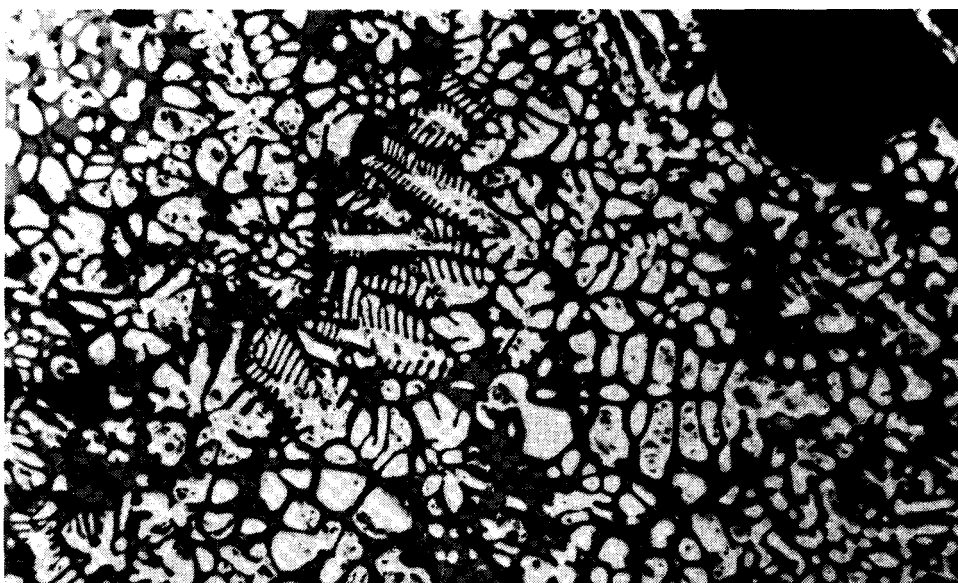


Fig. 5—A slag prepared in the laboratory showing dendrites of wustite in a fayalite matrix (polished, 120x)

since the sample consisted of fragments of the tip of the tuyère. This sample must therefore have been very near the hottest part of the furnace, yet the phases indicate that the tip of the tuyère attained a temperature not much in excess of 1250°C.

It appears to be a reasonable assumption that the operating temperature of ancient smelting furnaces can be obtained by measurement of the melting point of the slag samples. High-temperature microscopy can be used for this purpose, and the sample can be heated in air in a finely comminuted form. However, such measurements can give erroneous results because they do not necessarily relate to the operating conditions. Also, during heating in air, the wustite oxidizes rapidly and the system is then a different one. Melting points can be estimated<sup>3, 4</sup> from the chemical composition of the slag, but they may not be related to the furnace operating temperature since equilibrium conditions were not attained. Clear evidence of this is the presence of  $\alpha$ -quartz in several samples of slag. Slag 2 (Table V) is particularly interesting since it contains free wustite as well as silica. Under favourable conditions, the two oxides would react readily to form fayalite.

In the laboratory measurement of slag melting points, the sample is forced to melt by increases in the temperature. The sample is finely ground and, at the high temperatures imposed, slag-forming reactions or melting occurs rapidly. In an actual furnace, the lumps of ore and silica flux are coarse, and, if the temperature is low, intimate mixing is not easy. Then, the kinetics of slag formation are not favourable, and solid material may co-exist with liquid or plastic material for prolonged periods of time.

The structures observed in the present slag samples have been observed by other investigators in studies of modern<sup>26</sup> and ancient<sup>4, 25</sup> smelting processes. The presence of oxide in the form of dendrites is clear evidence that the oxide was in solution at elevated temperature, and crystallized out of a liquid during cooling. Dendritic

shapes are not expected to appear in material that underwent a solid-solid transformation.

### Conclusion

- (1) No essential differences were found between the composition of 9 slag samples from the Early Iron Age site near Broederstroom and that of a number of samples from six Later Iron Age sites of the central and western Transvaal, Swaziland, and Botswana. This fact strengthens the concept of an iron-smelting technology that remained basically unchanged during the whole period of the South African Iron Age (4th to 19th century AD).
- (2) The composition of the slags found in the eastern and northern Transvaal is in some respects (contents of titanium, alkalies, and earth alkalies) different from that of slags found in other parts of the Transvaal and adjacent areas. The reason for such regional differences lies mainly in the characteristics of the raw materials (ore, fuel, etc.) used in the smelting process.
- (3) The analyses for slags and ores available from the Broederstroom site were used in the calculation of correlation ratios to find the ore sources for the slags produced at that site. There is a definite correlation between the slag found at the Broederstroom furnace site K (flow) and the ores taken at a nearby natural erosion gully. The correlation ratios from a number of other samples fall into typical groups, but the corresponding ore sources were not found.
- (4) The establishment of correlations between the thermal characteristics of slags and the operational temperatures in the furnaces in which such slags were formed proved to be a more difficult task than was expected. The plotting of graphs for liquidus temperatures and areas in quasi-ternary diagrams for the system FeO, SiO<sub>2</sub>, and anorthite appears to be an over-simplified method in view of the complex constitution of South African slags. Similarly, the

direct determination of liquidus (flow) temperatures by hot-stage microscopic techniques or differential thermal analysis may also give doubtful values because of secondary processes between the slag constituents when a sample of slag is heated up in the test instrument. The use of experimental techniques (full-scale smelting experiments) in which the heat distribution and slag-solidification temperatures in an experimental furnace are observed and measured may overcome these difficulties.

- (5) The majority of the slags examined microscopically show the presence of  $\alpha$ -SiO<sub>2</sub>, but not of cristobalite, indicating that they were never exposed to temperatures of more than 1250°C. The presence of  $\alpha$ -SiO<sub>2</sub> and of small amounts of cristobalite in some slags shows that they were formed at furnace temperatures somewhat higher than 1250°C.
- (6) An important aspect influencing the results of archaeo-metallurgical investigations is the statistical validity of the sampling methods and the accuracy of the testing methods used. These factors have to be taken into account in the planning, undertaking, and interpreting of archaeo-metallurgical work.

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## Groundwater

The Groundwater Division of the Geological Society of South Africa is to hold its Biennial Symposium, Ground Water '82, in Johannesburg from 5th to 7th July, 1982.

The object of the symposium is to promote the science and technology of groundwater by providing a forum for the dissemination of knowledge over a wide spectrum of professional and technical expertise in the groundwater field, to encourage interaction between specialists in the groundwater field and those with a more general interest,

and to stimulate international interest by inviting some overseas speakers to participate.

The topics include Resource evaluation and management, Pollution and hydrogeochemical studies, Mining and geotechnical aspects, Innovations and developments in geohydrology, and Recent developments in bore-hole technology.

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