Appendix A: Data obtained from Grau and Poggi used for calculation of equations and in figures

Table 44: Chemical analyses of Sorel slags (measured from Figure 2 in Grau and Poggi, 1978)

Equivalent TiO_2 [Total Ti expressed as TiO_2] (mass %)	FeO (mass %)	Ti_2O_3 (mass %)
69.1	14.5	15.2
69.1	15.5	16.5
71.6	13.1	16.8
71.6	13.3	17.7
72.2	12.0	17.6
73.2	12.7	17.3
73.6	10.5	21.4
74.4	10.9	22.5
74.5	9.6	19.9
75.6	8.9	24.2
75.8	8.9	19.9
77.5	9.3	27.3
79.0	6.9	29.4

Appendix B: Normalised elemental phase analyses results of various samples

- **Sample DB100 (Sample from tap stream) – Point analyses of the M_3O_5 phase (2 µm intervals)**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.92	0.47	0.24	0.20	0.36	35.01	55.85	6.86	0.06	0.01	0.01	0.01
Analysis 2	1.15	0.43	0.35	0.21	0.34	34.93	55.71	6.78	0.07	0.03	0.00	0.00
Analysis 3	0.44	0.47	0.21	0.23	0.33	35.10	56.30	6.85	0.07	0.00	0.00	0.01
Analysis 4	1.11	0.37	0.32	0.21	0.34	35.17	55.61	6.80	0.06	0.00	0.01	0.00
Analysis 5	0.81	0.40	0.18	0.24	0.34	35.16	55.92	6.87	0.06	0.00	0.01	0.02
Analysis 6	1.27	0.44	0.30	0.22	0.34	34.62	55.90	6.83	0.06	0.01	0.00	0.01
Analysis 7	0.54	0.39	0.26	0.23	0.33	35.99	55.47	6.66	0.06	0.05	0.01	0.01
Analysis 8	0.77	0.43	0.21	0.27	0.34	36.56	54.84	6.50	0.06	0.03	0.01	0.01
Analysis 9	0.85	0.39	0.20	0.25	0.34	36.33	54.32	7.24	0.06	0.01	0.00	0.01
Analysis 10	1.12	0.54	0.29	0.27	0.33	36.38	54.40	6.60	0.06	0.01	0.00	0.00
Analysis 11	0.42	0.44	0.28	0.28	0.37	36.25	55.18	6.72	0.05	0.00	0.01	0.01
Analysis 12	0.85	0.38	0.13	0.27	0.34	35.39	55.82	6.74	0.06	0.01	0.01	0.00
Analysis 13	0.64	0.45	0.28	0.25	0.35	35.22	55.86	6.88	0.06	0.00	0.01	0.01
Analysis 14	0.45	0.48	0.22	0.26	0.37	35.15	56.12	6.87	0.06	0.01	0.01	0.01
Average	0.81	0.43	0.25	0.24	0.34	35.52	55.52	6.80	0.06	0.01	0.01	0.01
Standard Deviation	0.28	0.05	0.06	0.03	0.01	0.64	0.61	0.17	0.00	0.01	0.00	0.00

Calculated composition (normalising O to 5): $Mg_{0.07}Al_{0.04}V_{0.01}Mn_{0.01}Ti_{2.61}Fe_{0.27}O_5$ ($M_{3.01}O_5$)

- **Sample DB152 (Sample from tap stream) – Point analyses of the M_3O_5 phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.12	1.01	0.06	0.13	0.23	35.70	60.97	1.75	0.02	0.00	0.00	0.00
Analysis 2	1.06	1.20	0.09	0.12	0.21	35.20	60.33	1.77	0.02	0.00	0.00	0.00
Analysis 3	0.78	1.06	0.08	0.13	0.22	35.35	60.55	1.80	0.02	0.00	0.00	0.00
Analysis 4	1.26	1.13	0.09	0.14	0.26	35.36	60.19	1.54	0.03	0.00	0.00	0.00

Analysis 5	1.26	1.07	0.14	0.14	0.25	35.54	60.03	1.53	0.03	0.00	0.00	0.00
Analysis 6	0.85	1.02	0.13	0.17	0.23	35.55	60.48	1.54	0.02	0.00	0.00	0.00
Analysis 7	0.07	0.93	0.05	0.17	0.23	36.23	60.73	1.55	0.02	0.00	0.00	0.00
Average	0.77	1.06	0.09	0.14	0.23	35.56	60.47	1.64	0.02	0.00	0.00	0.00
Standard Deviation	0.50	0.09	0.03	0.02	0.02	0.34	0.32	0.13	0.00	0.00	0.00	0.00

Calculated composition (normalising O to 5): $Mg_{0.07}Al_{0.09}V_{0.01}Mn_{0.01}Ti_{2.84}Fe_{0.07}O_5$ ($M_{3.09}O_5$)

- **Sample DB156 (Sample from tap stream) – Point analyses of the M_3O_5 phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.79	1.09	0.08	0.18	0.52	34.84	55.62	6.83	0.05	0.00	0.01	0.00
Analysis 2	1.04	1.15	0.12	0.24	0.40	34.96	56.00	6.03	0.04	0.00	0.01	0.00
Analysis 3	0.49	1.07	0.09	0.21	0.39	35.64	56.17	5.90	0.04	0.00	0.01	0.00
Analysis 4	0.76	0.98	0.16	0.19	0.38	35.42	57.21	4.84	0.04	0.00	0.00	0.00
Analysis 5	0.19	1.05	0.07	0.24	0.38	35.74	57.27	5.01	0.04	0.00	0.01	0.00
Analysis 6	0.00	1.13	0.11	0.29	0.26	35.99	57.71	4.49	0.02	0.00	0.00	0.00
Average	0.54	1.08	0.10	0.22	0.39	35.43	56.66	5.52	0.04	0.00	0.01	0.00
Standard Deviation	0.40	0.06	0.03	0.04	0.08	0.45	0.84	0.88	0.01	0.00	0.00	0.00

Calculated composition (normalising O to 5): $Mg_{0.05}Al_{0.08}V_{0.01}Mn_{0.01}Ti_{2.65}Fe_{0.20}O_5$ ($M_{3.00}O_5$)

- **Sample DB105 (Pellet treated at 800 °C for 384 hours) – Point analyses of the rim phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.29	0.32	0.02	0.13	0.56	31.04	12.87	54.75	0.01	0.00	0.03	0.00

Calculated composition (normalising O to 3): $Mg_{0.02}Al_{0.02}V_{0.00}Mn_{0.02}Ti_{0.42}Fe_{1.52}O_3$ ($M_{2.00}O_3$)

- **Sample DB115 (Pellet treated at 600 °C for 24 hours) – Point analyses of the core region**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.89	0.61	0.04	0.30	0.26	35.05	56.94	5.86	0.04	0.00	0.00	0.00
Analysis 2	1.12	0.54	0.06	0.28	0.22	35.02	56.79	5.93	0.04	0.00	0.00	0.00

Analysis 3	1.70	0.69	0.07	0.29	0.18	34.67	56.52	5.84	0.04	0.00	0.00	0.00
Analysis 4	1.14	0.68	0.09	0.31	0.20	34.87	56.79	5.87	0.04	0.00	0.00	0.00
Average	1.21	0.63	0.07	0.29	0.22	34.90	56.76	5.87	0.04	0.00	0.00	0.00
Standard Deviation	0.34	0.07	0.02	0.01	0.04	0.17	0.18	0.04	0.00	0.00	0.00	0.00

Calculated composition (normalising O to 5): $Mg_{0.10}Al_{0.05}V_{0.01}Mn_{0.01}Ti_{2.69}Fe_{0.21}O_5$ ($M_{3.07}O_5$)

- **Sample DB115 (Pellet treated at 600 °C for 24 hours) – Point analyses of the mantle zone**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.84	0.44	0.12	0.37	0.24	38.52	58.60	0.82	0.03	0.00	0.01	0.00
Analysis 2	1.49	0.41	0.11	0.38	0.25	38.30	58.38	0.63	0.03	0.00	0.01	0.00
Analysis 3	0.45	0.54	0.07	0.40	0.23	38.98	58.43	0.85	0.05	0.00	0.01	0.00
Average	0.92	0.47	0.10	0.39	0.24	38.60	58.47	0.76	0.04	0.00	0.01	0.00
Standard Deviation	0.53	0.07	0.03	0.02	0.01	0.34	0.12	0.12	0.01	0.00	0.00	0.00

Calculated composition (normalising O to 2): $Mg_{0.03}Al_{0.01}V_{0.01}Mn_{0.00}Ti_{1.01}Fe_{0.01}O_2$ ($M_{1.07}O_2$)

- **Sample DB115 (Pellet treated at 600 °C for 24 hours) – Point analyses of the rim phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.63	1.55	0.07	0.06	0.11	30.42	4.14	62.83	0.01	0.13	0.01	0.03
Analysis 2	0.09	0.92	0.00	0.05	0.32	29.04	2.72	66.81	0.01	0.00	0.01	0.04
Average	0.36	1.23	0.04	0.05	0.22	29.73	3.43	64.82	0.01	0.06	0.01	0.04
Standard Deviation	0.39	0.45	0.05	0.01	0.15	0.98	1.00	2.81	0.00	0.09	0.00	0.01

Calculated composition (normalising O to 3): $Mg_{0.02}Al_{0.06}V_{0.00}Mn_{0.01}Ti_{0.29}Fe_{1.64}O_3$ ($M_{2.02}O_3$)

- **Sample DB125 (Pellet treated at 400 °C for 384 hours) – Point analyses of the bulk phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.30	0.52	0.12	0.37	0.21	36.81	55.14	6.49	0.03	0.00	0.01	0.00
Analysis 2	0.92	0.51	0.08	0.38	0.17	36.83	54.85	6.23	0.03	0.00	0.01	0.00
Average	0.61	0.52	0.10	0.38	0.19	36.82	55.00	6.36	0.03	0.00	0.01	0.00

Standard Deviation	0.44	0.01	0.03	0.00	0.03	0.02	0.21	0.18	0.00	0.00	0.00	0.00

Calculated composition (normalising O to 5): $Mg_{0.05}Al_{0.04}V_{0.01}Mn_{0.01}Ti_{2.50}Fe_{0.22}O_5$ ($M_{2.83}O_5$)

- **Sample DB125 (Pellet treated at 400 °C for 384 hours) – Point analyses of the lamellae present in the bulk phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.10	0.36	0.14	0.31	0.05	38.36	60.03	0.62	0.02	0.00	0.00	0.00
Analysis 2	0.34	0.38	0.09	0.41	0.01	38.28	60.15	0.31	0.02	0.00	0.01	0.01
Average	0.22	0.37	0.11	0.36	0.03	38.32	60.09	0.47	0.02	0.00	0.01	0.00
Standard Deviation	0.17	0.02	0.03	0.07	0.03	0.06	0.08	0.22	0.00	0.00	0.00	0.00

Calculated composition (normalising O to 2): $Mg_{0.01}Al_{0.01}V_{0.01}Mn_{0.00}Ti_{1.04}Fe_{0.01}O_2$ ($M_{1.08}O_2$)

- **Sample DB132 (Block sample treated at 400 °C for 384 hours) – Point analyses of the M_3O_5 phase**

	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.36	0.39	0.40	0.15	0.83	35.11	47.72	14.95	0.06	0.00	0.03	0.00
Analysis 2	0.56	0.37	0.38	0.13	0.77	34.95	47.80	14.95	0.07	0.00	0.02	0.00
Analysis 3	0.68	0.38	0.28	0.19	0.76	35.29	47.39	14.96	0.06	0.00	0.01	0.00
Analysis 4	0.49	0.37	0.45	0.12	0.96	34.99	47.09	15.44	0.06	0.00	0.02	0.01
Average	0.52	0.38	0.38	0.14	0.83	35.09	47.50	15.07	0.06	0.00	0.02	0.00
Standard Deviation	0.13	0.01	0.07	0.03	0.09	0.15	0.33	0.24	0.00	0.00	0.01	0.00

Calculated composition (normalising O to 5): $Mg_{0.04}Al_{0.03}Zr_{0.01}V_{0.01}Mn_{0.03}Ti_{2.29}Fe_{0.55}O_5$ ($M_{2.96}O_5$)

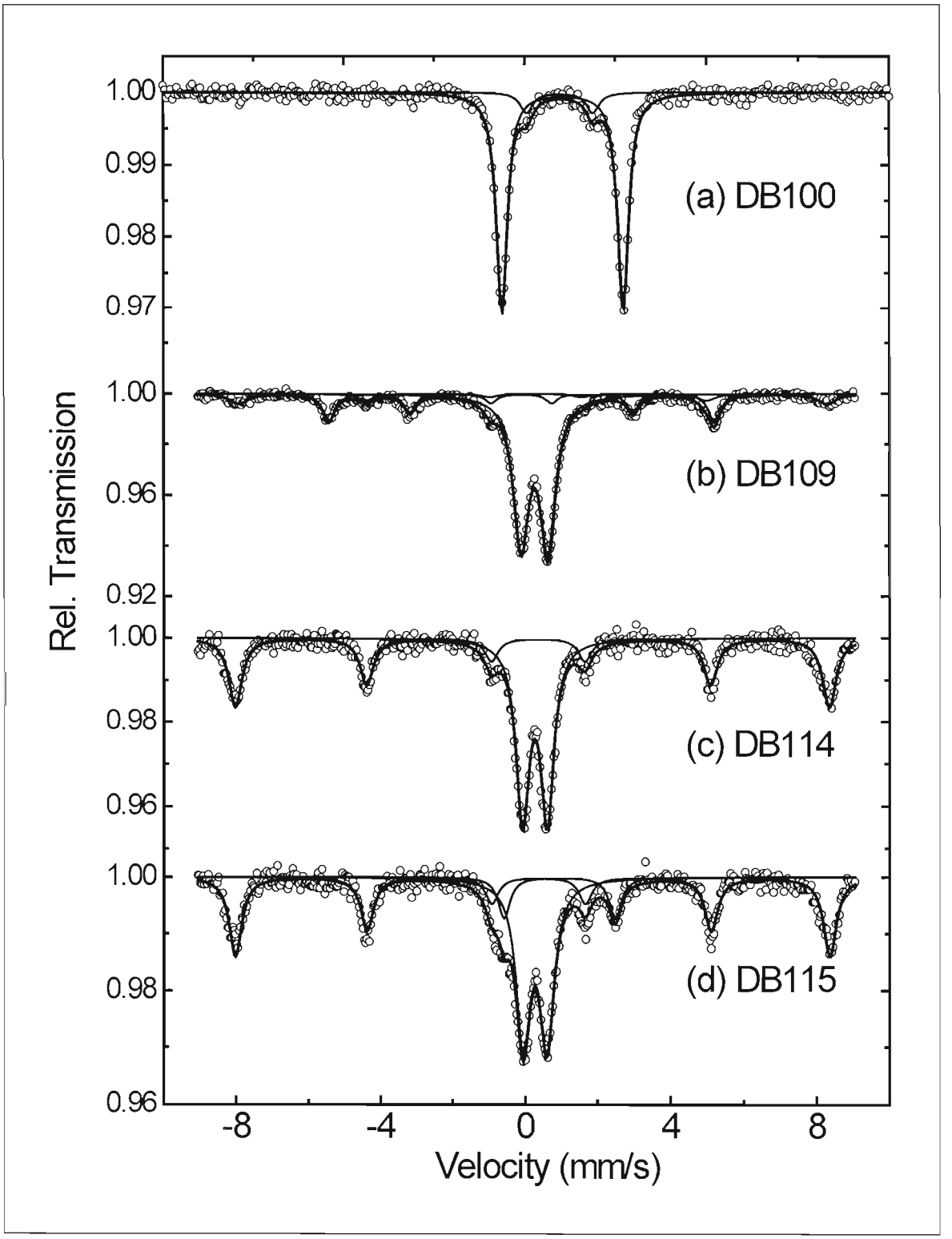
- **Sample DB132 (Block sample treated at 400 °C for 384 hours) – Point analyses of the TiO_2 phase**

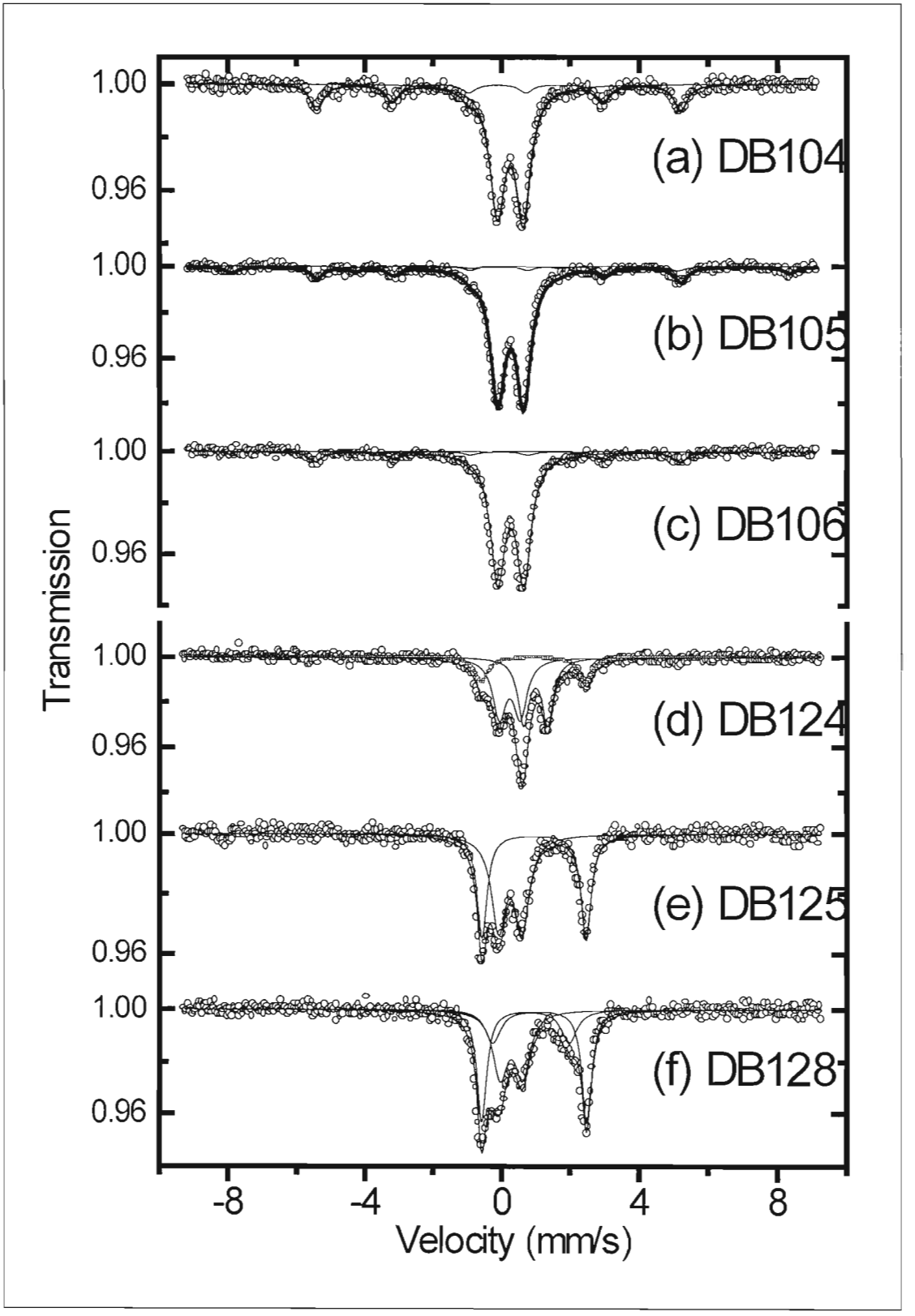
	Analysis (mass per cent)											
	Mg	Al	Zr	V	Mn	O	Ti	Fe	Cr	Si	Ca	S
Analysis 1	0.00	0.02	0.52	0.10	0.00	39.80	59.44	0.07	0.04	0.00	0.00	0.00
Analysis 2	0.20	0.00	0.54	0.15	0.00	38.94	60.11	0.01	0.04	0.00	0.00	0.00
Analysis 3	0.00	0.01	0.58	0.09	0.01	38.67	60.59	0.00	0.04	0.00	0.00	0.00
Analysis 4	0.00	0.01	0.59	0.13	0.01	38.84	60.36	0.00	0.04	0.00	0.00	0.00
Average	0.05	0.01	0.56	0.12	0.01	39.06	60.13	0.02	0.04	0.00	0.00	0.00

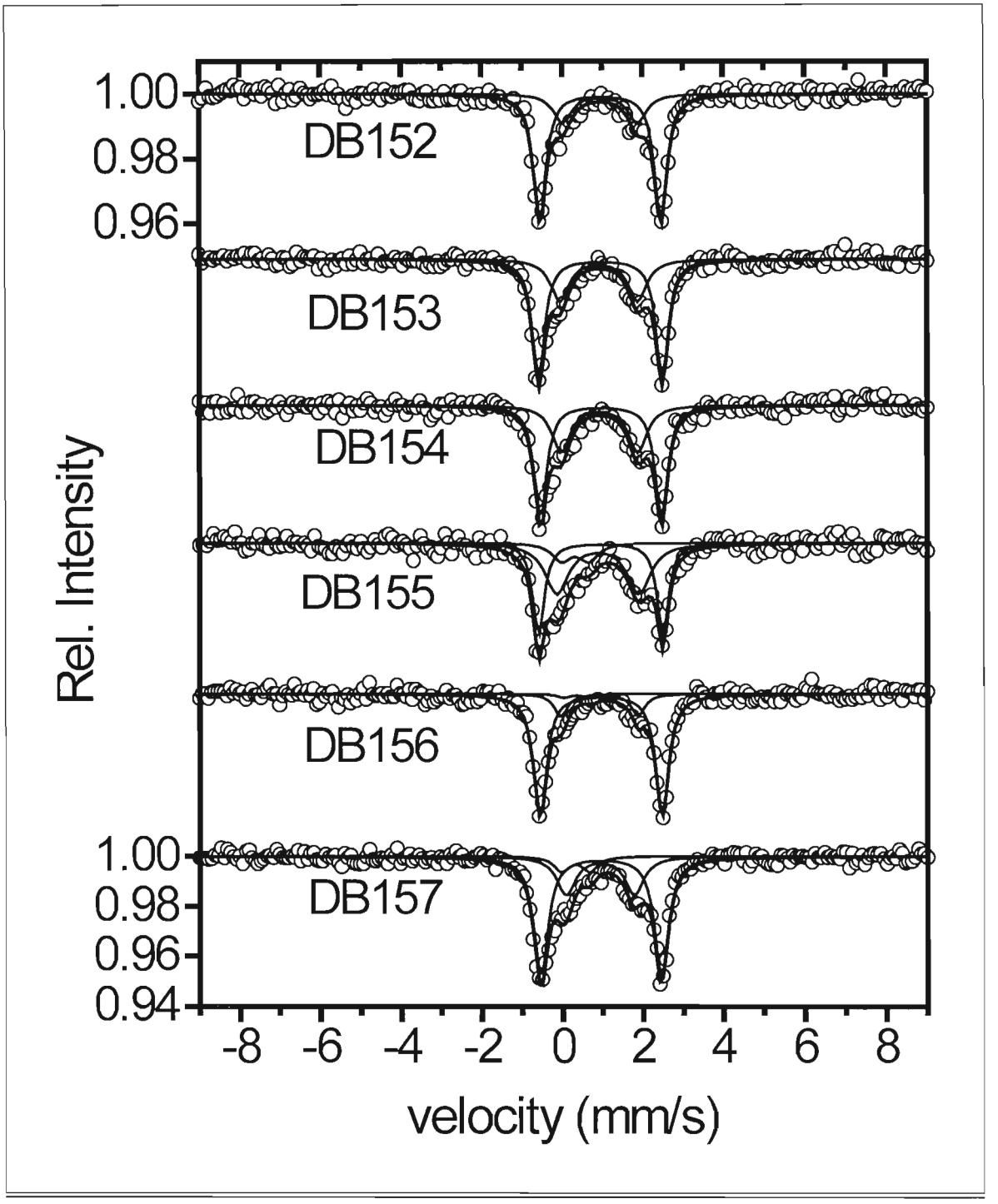
Standard Deviation	0.10	0.01	0.03	0.03	0.01	0.50	0.50	0.03	0.00	0.00	0.00	0.00

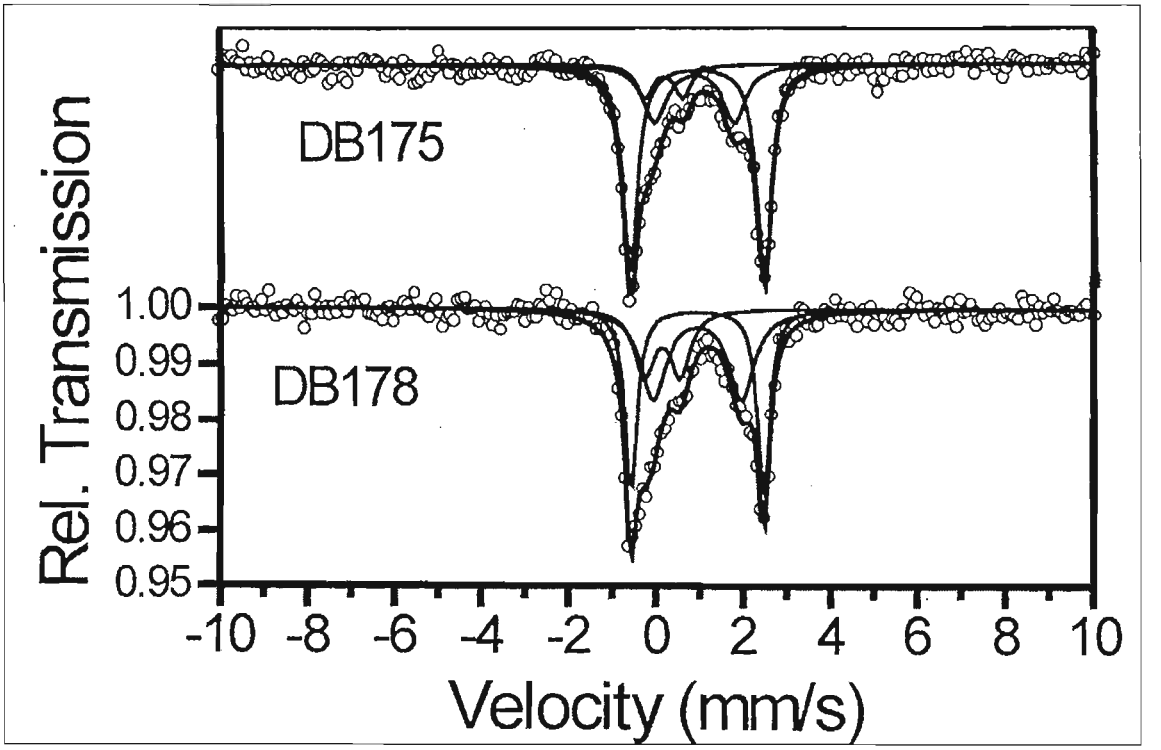
Calculated composition (normalising O to 2): $Ti_{1.03}O_2$ ($M_{1.03}O_2$)

Appendix C: Mössbauer spectra of samples in this study




Transmission
1.00
0.96
(a) DB104
(b) DB105
(c) DB106
(d) DB124
(e) DB125
(f) DB128
-8
-4
0
4
8
Velocity (mm/s)


1.00
0.98
0.96
DB152
DB153
DB154
DB155
DB156
1.00
0.98
0.96
0.94
DB157
Rel. Intensity
-8
-6
-4
-2
0
2
4
6
8
velocity (mm/s)

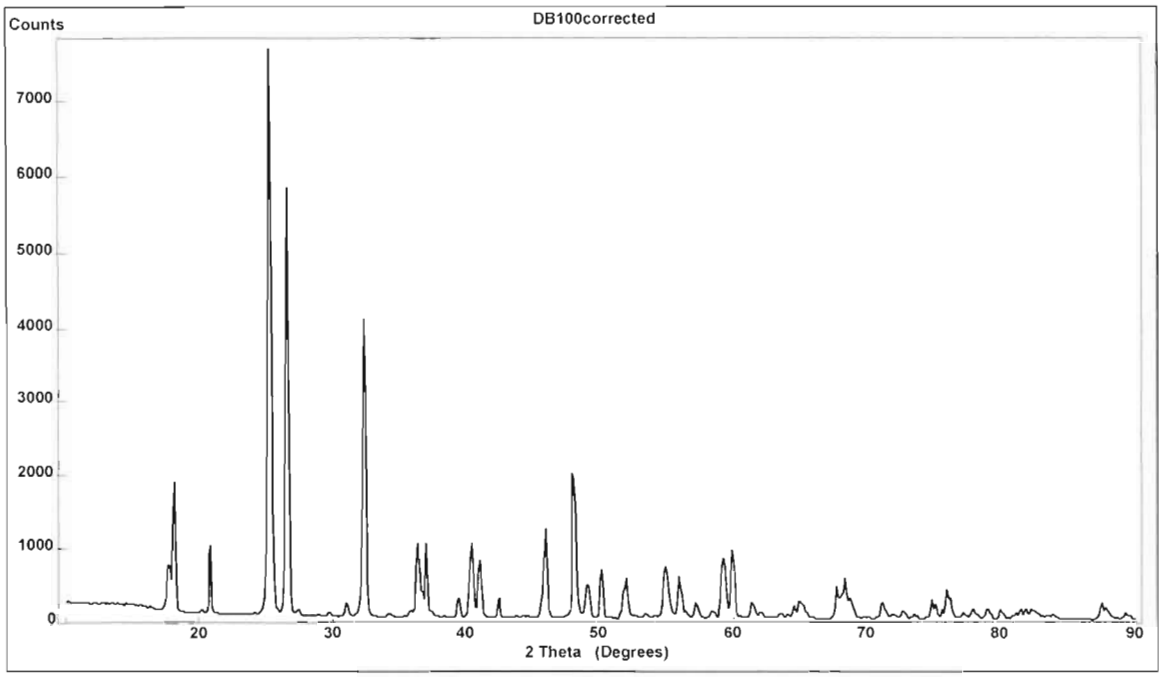

DB175
DB178
Rel. Transmission
1.00
0.99
0.98
0.97
0.96
0.95
-10
-8
-6
-4
-2
0
2
4
6
8
10
Velocity (mm/s)

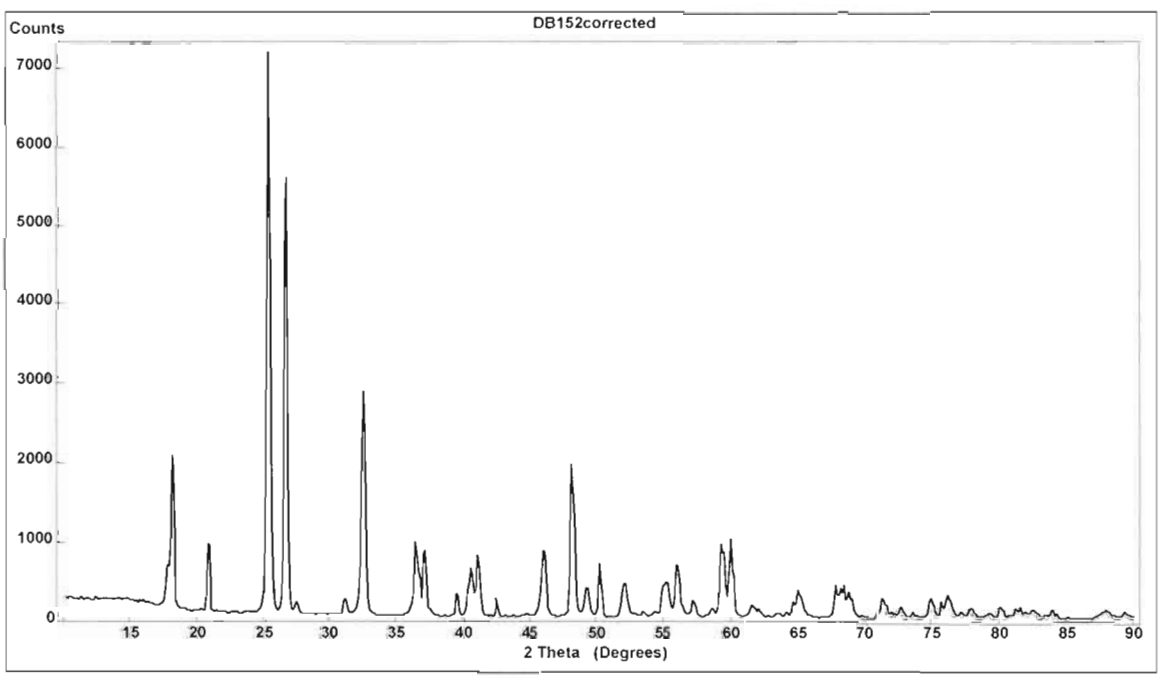
Appendix D: Crystallographic data for sample DB156

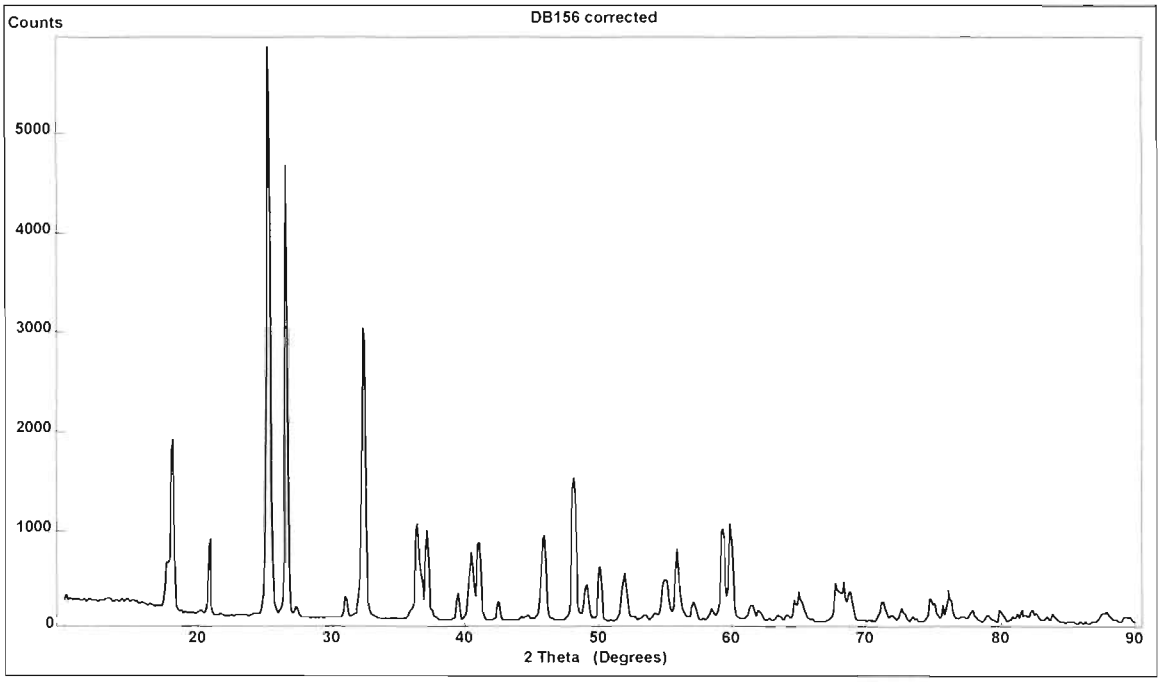
h	k	l	d (Å)	I/I_0 (obs)	I/I_0 (calc)	h	k	l	d (Å)	I/I_0 (obs)	I/I_0 (calc)
0	0	2	5.015	9.8	6.6	2	0	6	1.579	2.9	2.9
0	0	2	5.003	4.7	3.3	2	0	6	1.575	1.6	1.4
2	0	0	4.910	36.0	40.7	2	2	3	1.559	21.0	20.2
2	0	0	4.898	16.9	20.2	3	1	5	1.556	9.2	9.4
1	1	0	3.531	100.0	100.0	2	2	3	1.555	9.9	10.0
1	1	0	3.522	51.5	49.7	3	1	5	1.552	4.5	4.7
2	0	2	3.505	11.6	11.4	5	1	3	1.543	18.0	17.0
2	0	2	3.497	5.5	5.7	5	1	3	1.539	7.9	8.5
1	1	1	3.330	11.0	11.0	1	1	6	1.508	4.5	4.6
1	1	1	3.322	4.9	5.5	1	1	6	1.504	2.1	2.3
1	1	2	2.885	5.9	3.8	4	2	0	1.496	2.4	2.9
1	1	2	2.878	2.9	1.9	4	2	0	1.493	1.0	1.5
2	0	3	2.760	79.2	71.7	6	0	3	1.467	1.0	1.6
2	0	3	2.753	39.1	35.7	2	2	4	1.441	4.3	4.7
0	0	4	2.504	2.8	2.6	2	2	4	1.438	2.2	2.3
0	0	4	2.498	1.4	1.3	4	2	2	1.434	6.6	6.4
3	1	0	2.473	20.9	21.0	4	2	2	1.430	3.0	3.2
3	1	0	2.467	11.1	10.4	5	1	4	1.428	2.5	2.7
4	0	0	2.451	7.2	7.3	5	1	4	1.425	1.0	1.3
4	0	0	2.445	3.4	3.6	3	1	6	1.383	5.6	4.8
1	1	3	2.425	20.8	22.6	3	1	6	1.379	2.4	2.4
1	1	3	2.419	9.6	11.3	2	0	7	1.372	3.1	3.5
3	1	1	2.401	1.4	1.4	2	0	7	1.369	1.5	1.7
2	0	4	2.230	15.1	14.1	4	2	3	1.365	7.4	8.5
2	0	4	2.224	8.2	7.0	4	2	3	1.362	3.6	4.2
3	1	2	2.217	2.1	1.7	1	1	7	1.325	2.2	2.7
3	1	2	2.211	1.0	0.9	2	2	5	1.323	4.2	5.0
4	0	2	2.201	18.8	15.8	1	1	7	1.322	1.1	1.3
4	0	2	2.196	9.7	7.8	2	2	5	1.320	2.1	2.5
1	1	4	2.041	1.0	0.2	7	1	1	1.301	3.8	5.5
3	1	3	1.987	4.6	4.5	7	1	1	1.298	1.8	2.7
3	1	3	1.982	2.4	2.2	7	1	2	1.270	6.7	5.3
4	0	3	1.975	21.0	20.4	7	1	2	1.266	3.3	2.7
4	0	3	1.970	10.4	10.2	6	0	5	1.265	2.7	2.3
0	2	0	1.890	35.1	33.3	6	0	5	1.262	1.4	1.1
0	2	0	1.886	18.1	16.6	0	2	6	1.250	8.0	6.4
2	0	5	1.853	10.9	9.0	1	3	0	1.249	3.2	2.7
2	0	5	1.849	5.7	4.5	0	2	6	1.247	3.8	3.2
2	2	0	1.764	3.9	3.5	1	3	0	1.246	1.6	1.3
2	2	0	1.759	1.9	1.7	3	1	7	1.237	1.0	1.0
3	1	4	1.759	10.4	9.7	6	2	1	1.226	3.2	2.7
3	1	4	1.754	5.1	4.8	6	2	1	1.223	1.4	1.4
5	1	1	1.714	1.5	0.5	2	2	6	1.212	2.0	1.7

0	0	6	1.668	11.0	10.9	2	2	6	1.209	1.0	0.9
0	0	6	1.664	6.1	5.4	8	0	2	1.189	2.2	1.5
2	2	2	1.663	2.1	1.8	8	0	2	1.187	1.7	0.8
2	2	2	1.659	1.0	0.9	3	3	0	1.175	2.6	1.6
5	1	2	1.644	20.0	19.3	3	3	0	1.172	1.4	0.8
5	1	2	1.639	10.0	9.6	1	3	3	1.170	3.6	2.0
6	0	0	1.633	1.3	1.0	1	3	3	1.167	1.9	1.0
6	0	1	1.612	5.0	4.3	6	2	3	1.158	2.7	1.5
6	0	1	1.608	2.5	2.1	6	2	3	1.156	1.6	0.7

Appendix E: X-ray diffraction patterns of the slag samples shown in Table 12






DB156 corrected
Counts
5000
4000
3000
2000
1000
0
20
30
40
50
60
70
80
90
2 Theta (Degrees)

Appendix F: Normalised oxide phase analyses results of various samples

- **Sample YS2872 (Air-cooled spoon sample from tap stream) – Dark coloured glass phase**

	Analysis (mass per cent)								
	MgO	Al_2O_3	TiO_2	MnO	FeO	SiO_2	K_2O	CaO	Na_2O
Analysis 1	-	2.83	8.72	0.44	1.75	83.40	1.20	1.01	0.65
Analysis 2	-	3.03	7.15	0.76	1.62	84.38	0.84	1.32	0.91
Analysis 3	-	3.52	8.77	0.64	1.86	83.05	1.27	0.89	-
Average	-	3.13	8.21	0.61	1.74	83.61	1.10	1.07	0.78
Standard Deviation	-	0.36	0.92	0.16	0.12	0.69	0.23	0.22	0.18

- **Sample YS2872 (Air-cooled spoon sample from tap stream) – Light coloured glass phase**

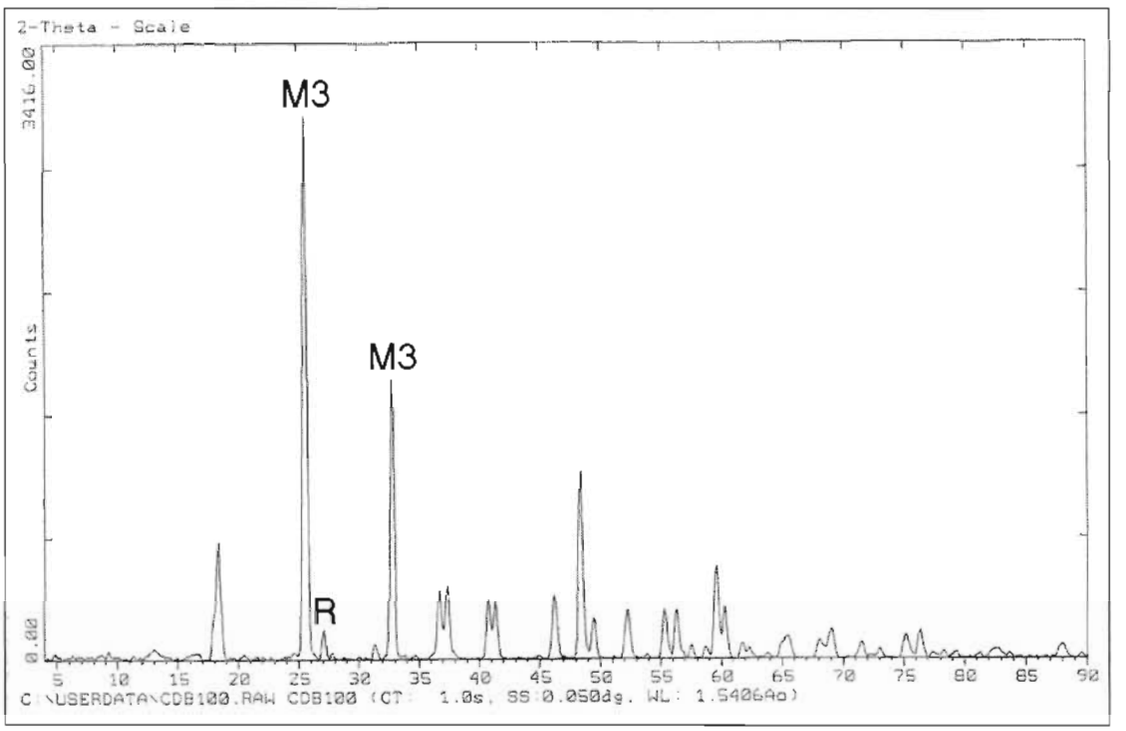
	Analysis (mass per cent)								
	MgO	Al_2O_3	TiO_2	MnO	FeO	SiO_2	K_2O	CaO	Na_2O
Analysis 1	-	6.41	11.17	9.61	7.34	48.75	0.23	16.49	-
Analysis 2	-	5.99	12.53	10.65	6.29	46.59	0.10	17.84	-
Analysis 3	-	5.82	10.11	11.30	16.68	43.88	0.07	12.14	-
Analysis 4	-	5.17	12.11	11.47	14.46	44.07	-	12.72	-
Average	-	5.85	11.48	10.76	11.19	45.82	0.13	14.80	-
Standard Deviation	-	0.52	1.08	0.84	5.15	2.31	0.09	2.80	-

APPENDIX G: X-ray diffraction patterns for the pellet samples

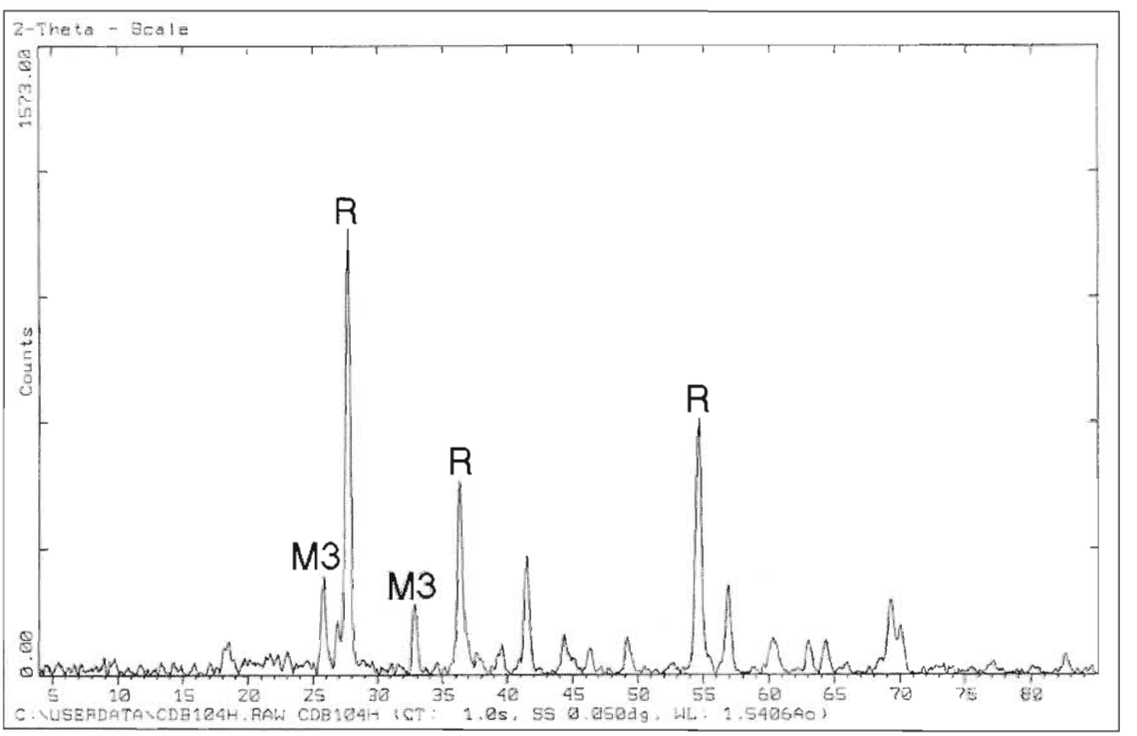
The following abbreviations are used for the identification of phases:

M3 – M_3O_5 phase R – Rutile H – Hematite
M6 – M_6O_{11} phase A – Anatase

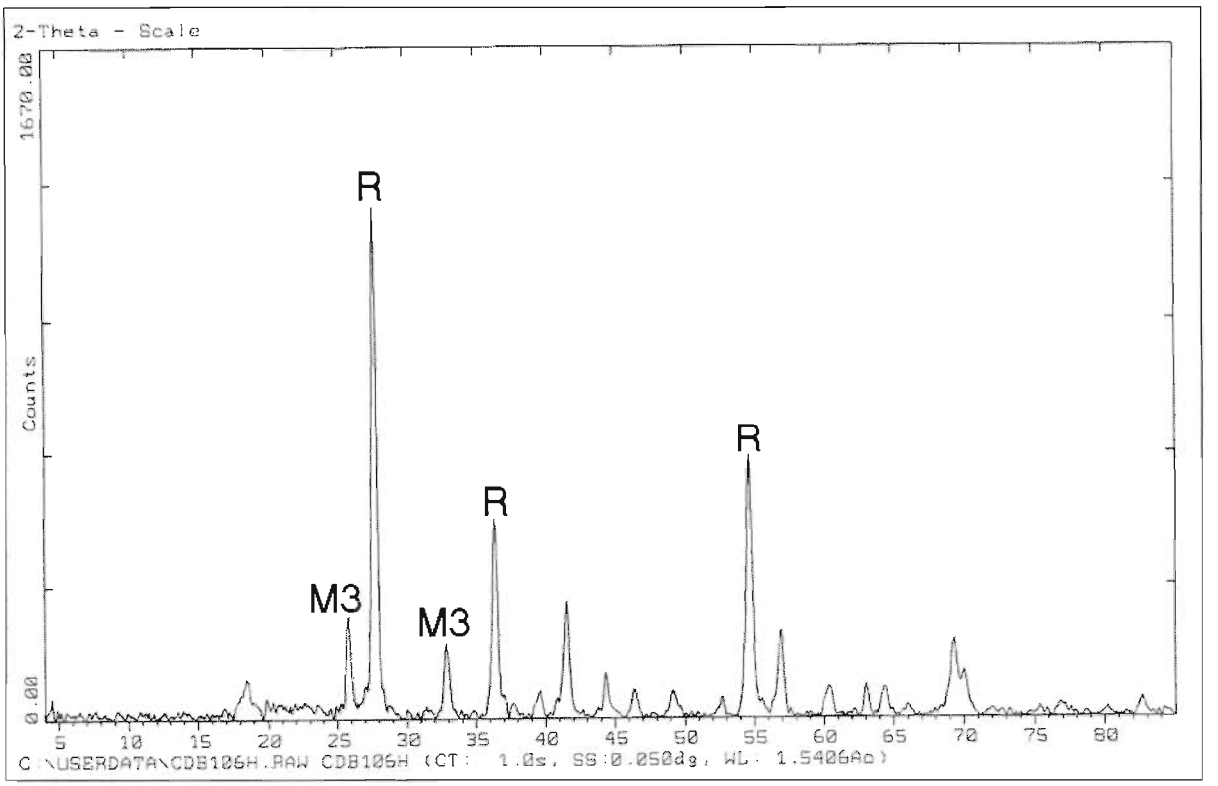
Sample DB100: Starting material for tests with pellets



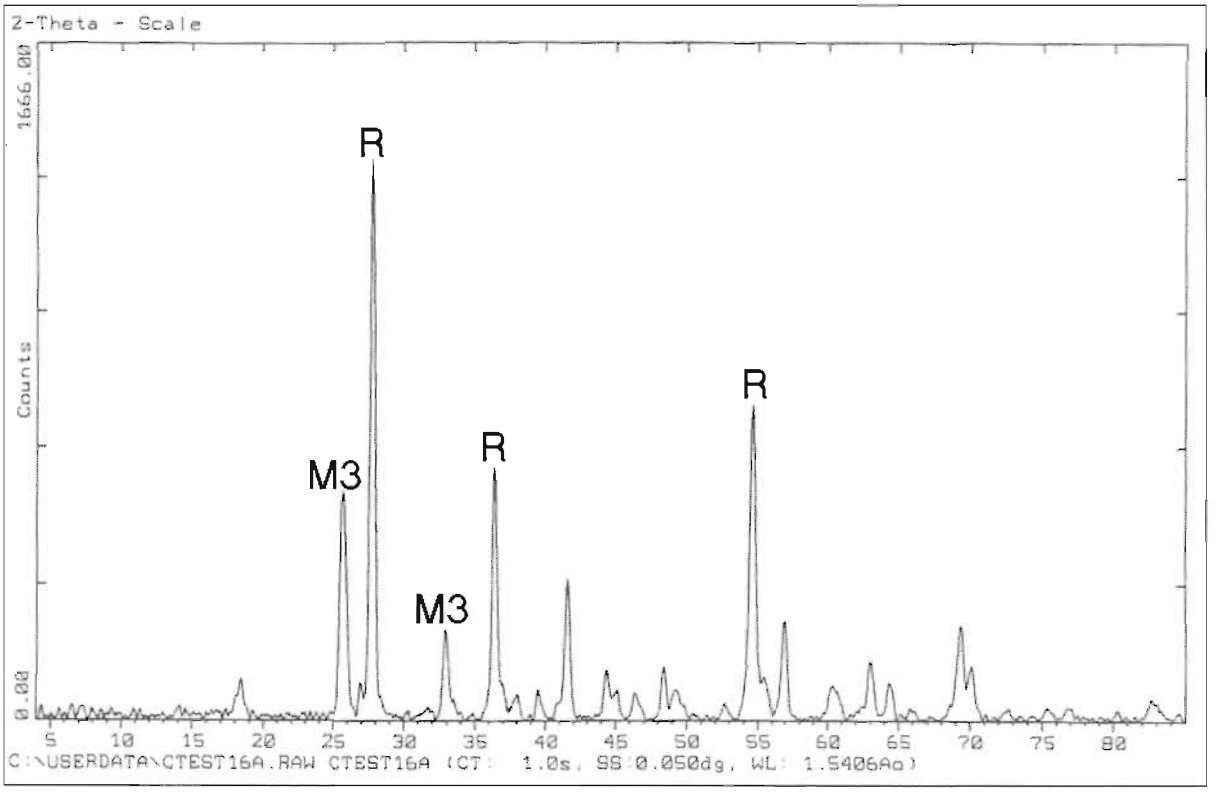
Sample DB104: Pellet; 1000 °C; 24 hours



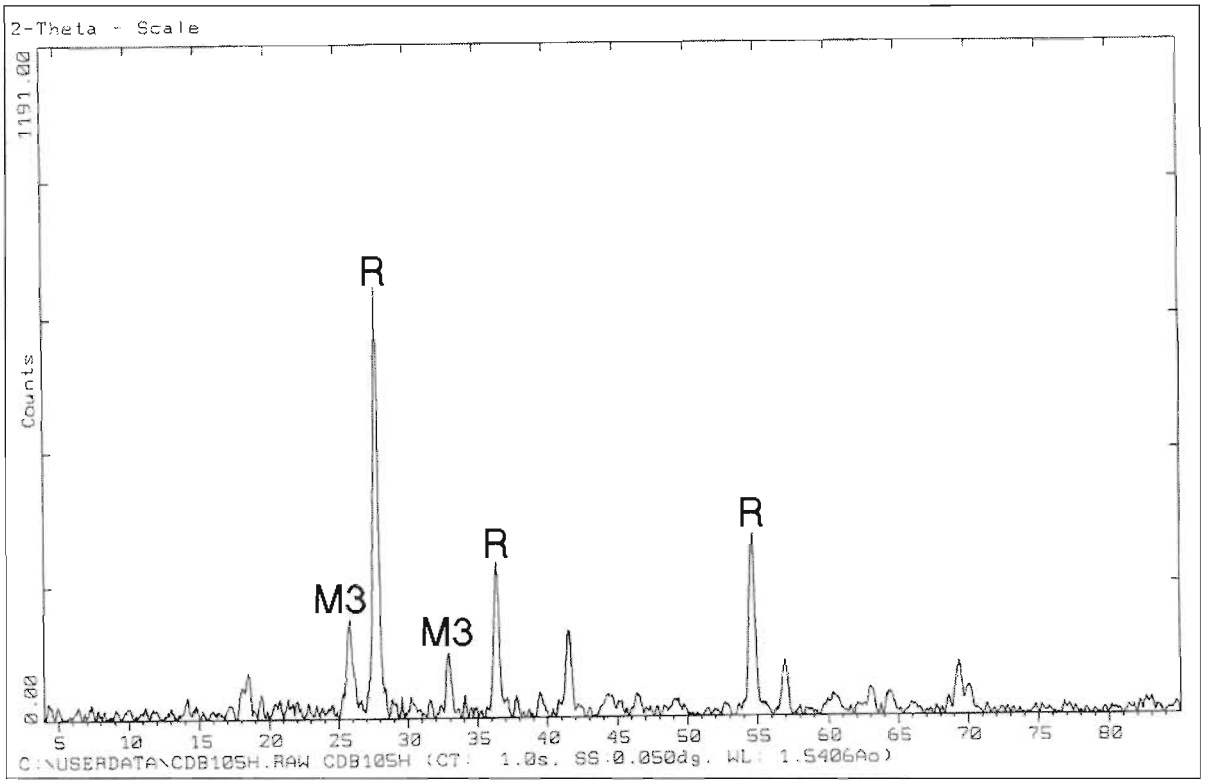
Sample DB106: Pellet; 1000 °C; 384 hours



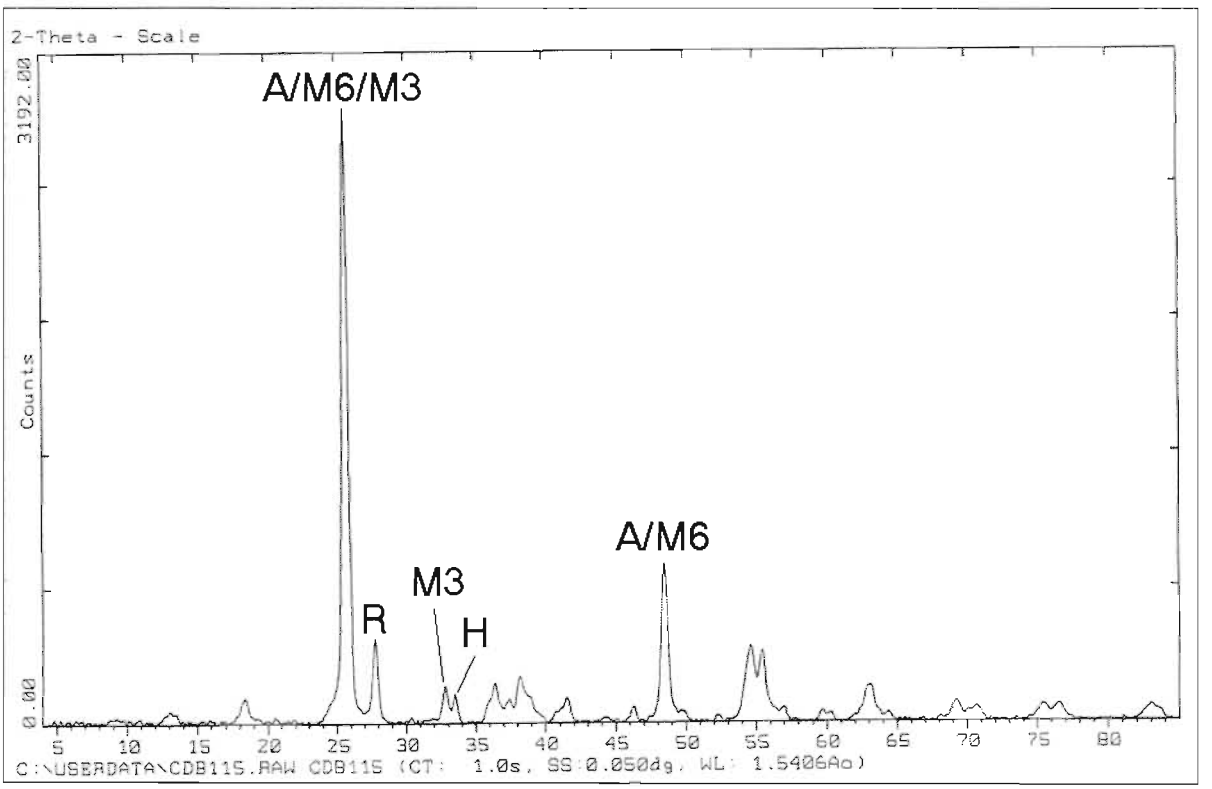
Sample DB109: Pellet; 800 °C; 24 hours



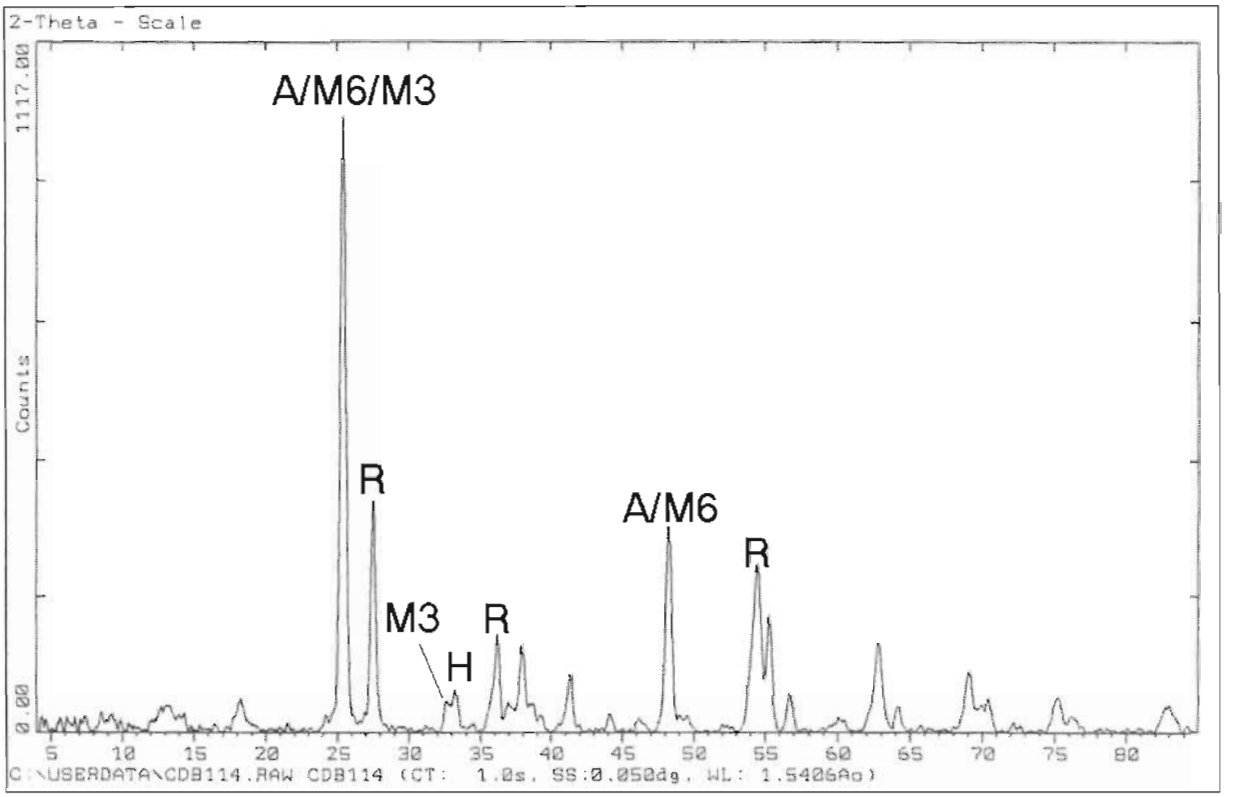
Sample DB105: Pellet; 800 °C; 384 hours



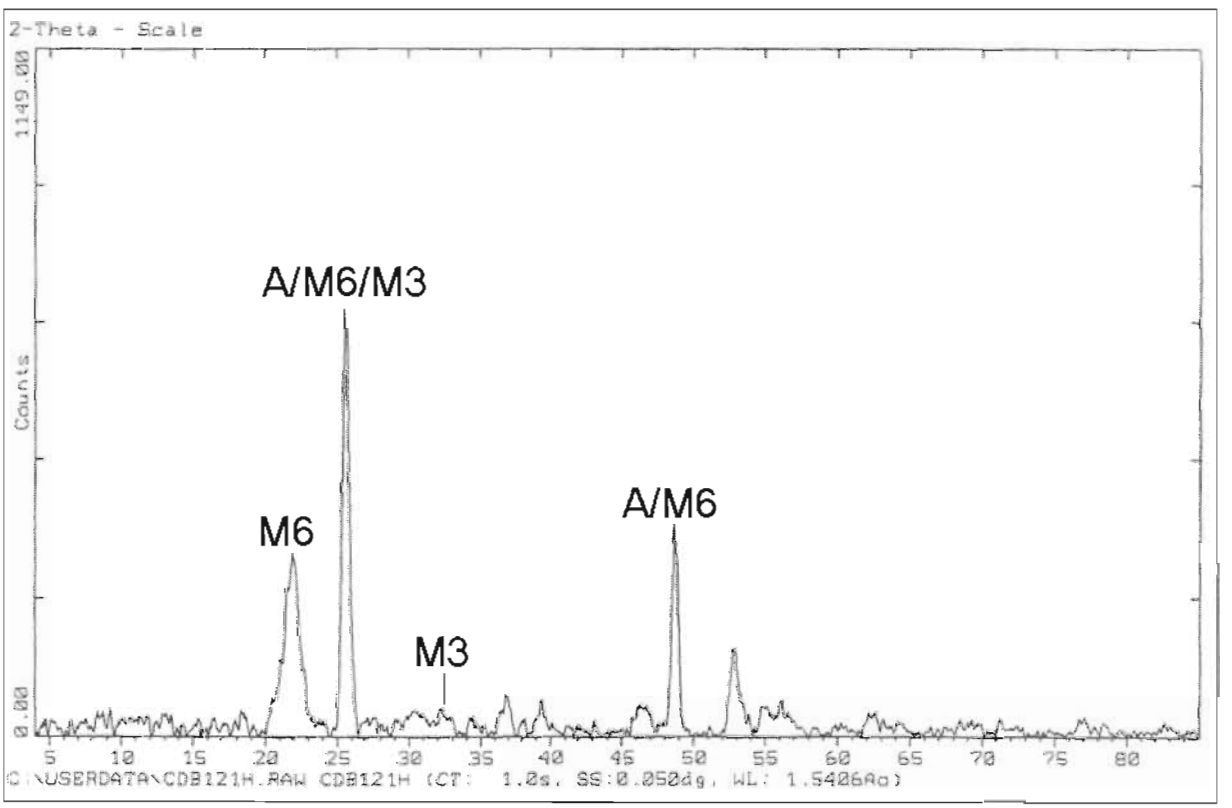
Sample DB115: Pellet; 600 °C; 24 hours



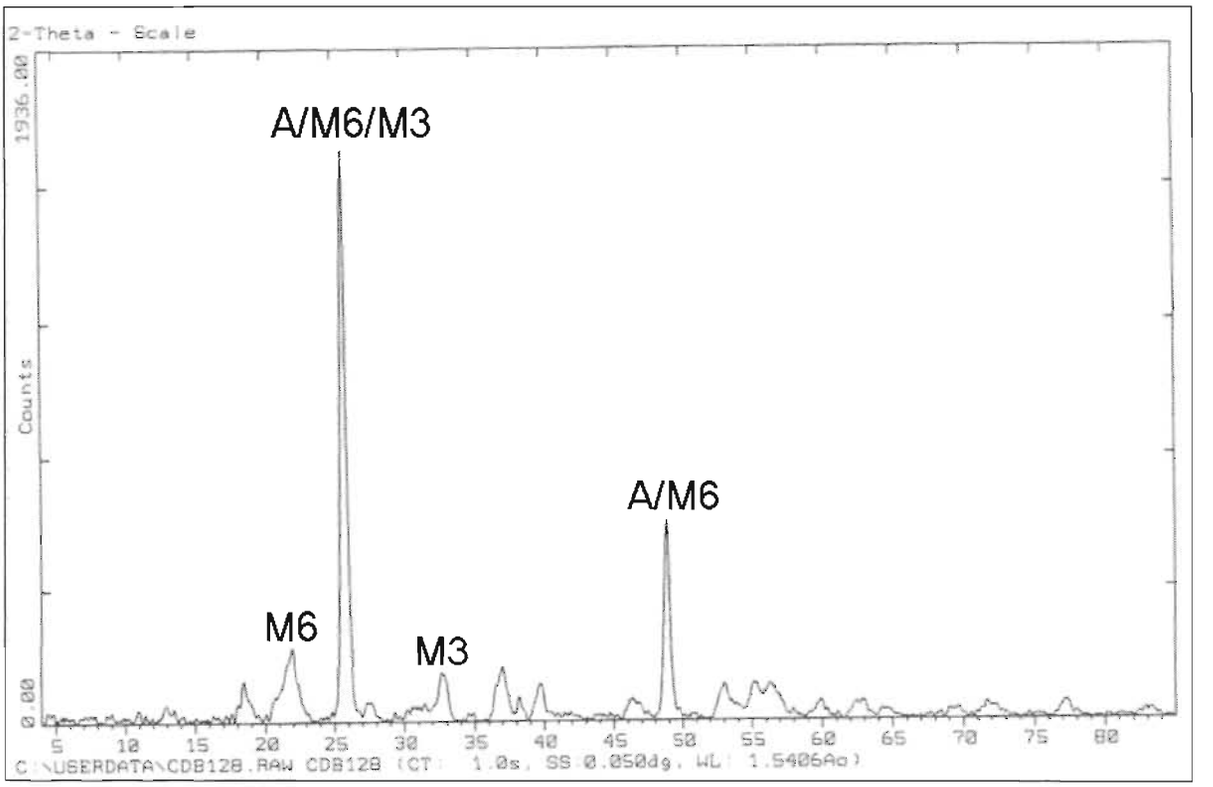
Sample DB114: Pellet; 600 °C; 384 hours



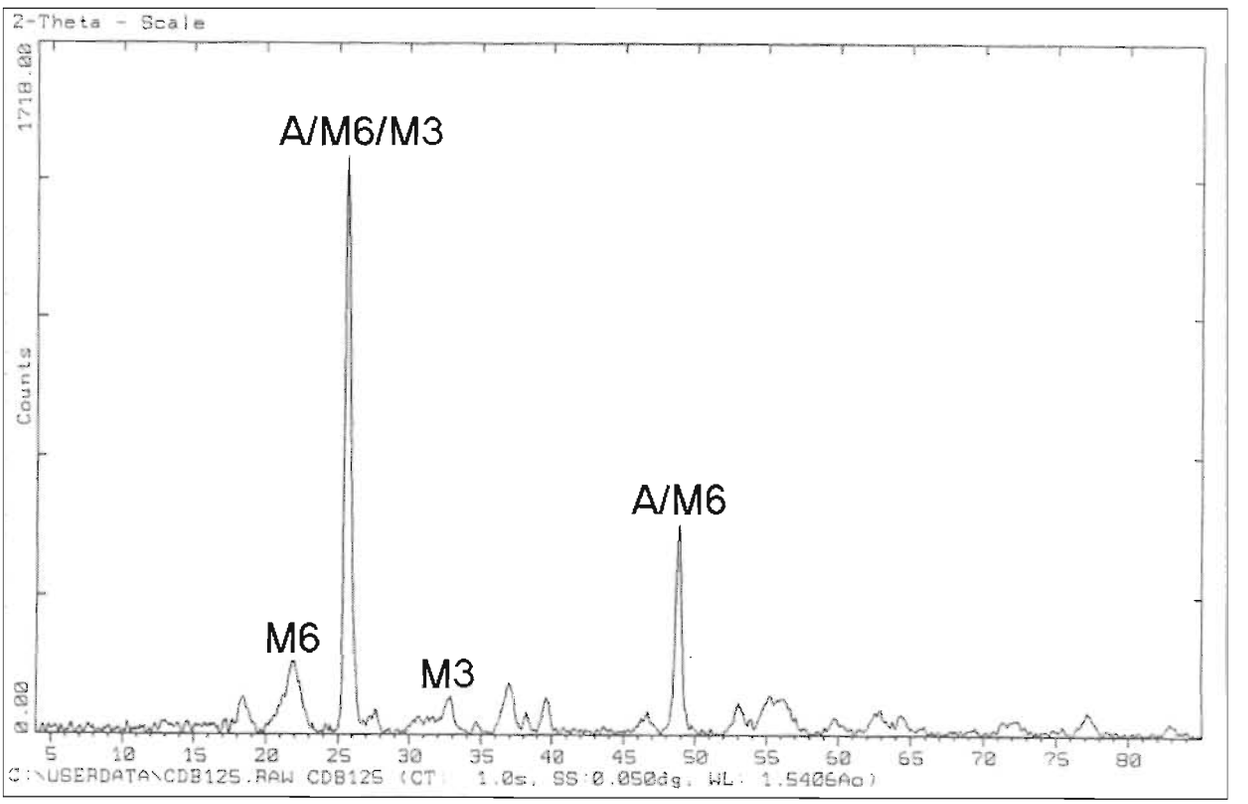
Sample DB121: Pellet; 400 °C; 24 hours



Sample DB128: Pellet; 400 °C; 48 hours



Sample DB125: Pellet; 400 °C; 384 hours



Appendix H: Calculation of the composition and cation oxidation states for sample DB125 (bulk phase)

From the X-ray diffraction results for this sample we know that both M_6O_{11} and anatase phases are present. According to Grey, Cranswick, et. al. (2000) the M_6O_{11} structure comprises planar intergrowth of M_3O_5 compositional blocks with the pseudobrookite-type structure and MO_2 compositional blocks with the anatase-type structure. The calculations were therefore carried out to write the compositions in these terms. The M_3O_5 phase was calculated in terms of the solid solution end members. Various scenarios were calculated based on the given assumptions.

Calculation 1

Assumptions:

- All the iron is present as Fe^{2+}.
- The O content as given in Appendix B is correct.

Based on the assumptions the following composition can be calculated:

$$0.56\left[Ti^{4+}_{1.00}O^{2-}_{2}\right] \bullet 0.25\left[Ti^{4+}_{1.00}\left(V^{3+}_{0.03}Al^{3+}_{0.10}Ti^{3+}_{1.87}\right)O^{2-}_{5}\right] \bullet 0.19\left[\left(Mg^{2+}_{0.18}Mn^{2+}_{0.04}Fe^{2+}_{0.78}\right)Ti^{4+}_{2}O^{2-}_{5}\right]$$

Calculation 2

Assumptions:

- The Mössbauer data from Table 27 is used for the calculation of the oxidation state of iron.
- The O content as given in Appendix B is correct.

Based on the assumptions the following composition can be calculated:

$$0.56\left[Ti^{4+}_{1.00}O^{2-}_{2}\right] \bullet 0.29\left[Ti^{4+}_{1.00}\left(V^{3+}_{0.02}Al^{3+}_{0.09}Ti^{3+}_{1.89}\right)O^{2-}_{5}\right] \bullet 0.11\left[\left(Mg^{2+}_{0.31}Mn^{2+}_{0.06}Fe^{2+}_{0.63}\right)Ti^{4+}_{2}O^{2-}_{5}\right] \bullet 0.04\left[Fe^{3+}_{2.00}Ti^{4+}_{1.00}O^{2-}_{5}\right]$$

Calculation 3

Assumptions:

- The Mössbauer data from Table 27 is used for the calculation of the oxidation state of iron.
- The oxygen content as given in Appendix B is incorrect, with the oxygen content underestimated by 2 per cent. Based on this the composition of the phase changes from $Mg_{0.05}Al_{0.04}V_{0.01}Mn_{0.01}Ti_{2.50}Fe_{0.22}O_5$ ($M_{2.83}O_5$) to $Mg_{0.05}Al_{0.04}V_{0.01}Mn_{0.01}Ti_{2.38}Fe_{0.21}O_5$ ($M_{2.70}O_5$), with the oxygen content normalised to 5 in both instances.

Based on the assumptions the following composition can be calculated:

$$0.79\left[Ti^{4+}_{1.00}O^{2-}_{2}\right] \bullet 0.10\left[Ti^{4+}_{1.00}\left(V^{3+}_{0.05}Al^{3+}_{0.21}Ti^{3+}_{1.74}\right)O^{2-}_{5}\right] \bullet 0.08\left[\left(Mg^{2+}_{0.33}Mn^{2+}_{0.07}Fe^{2+}_{0.60}\right)Ti^{4+}_{2}O^{2-}_{5}\right] \bullet 0.03\left[Fe^{3+}_{2.00}Ti^{4+}_{1.00}O^{2-}_{5}\right]$$

The following comments can be made on these calculations:

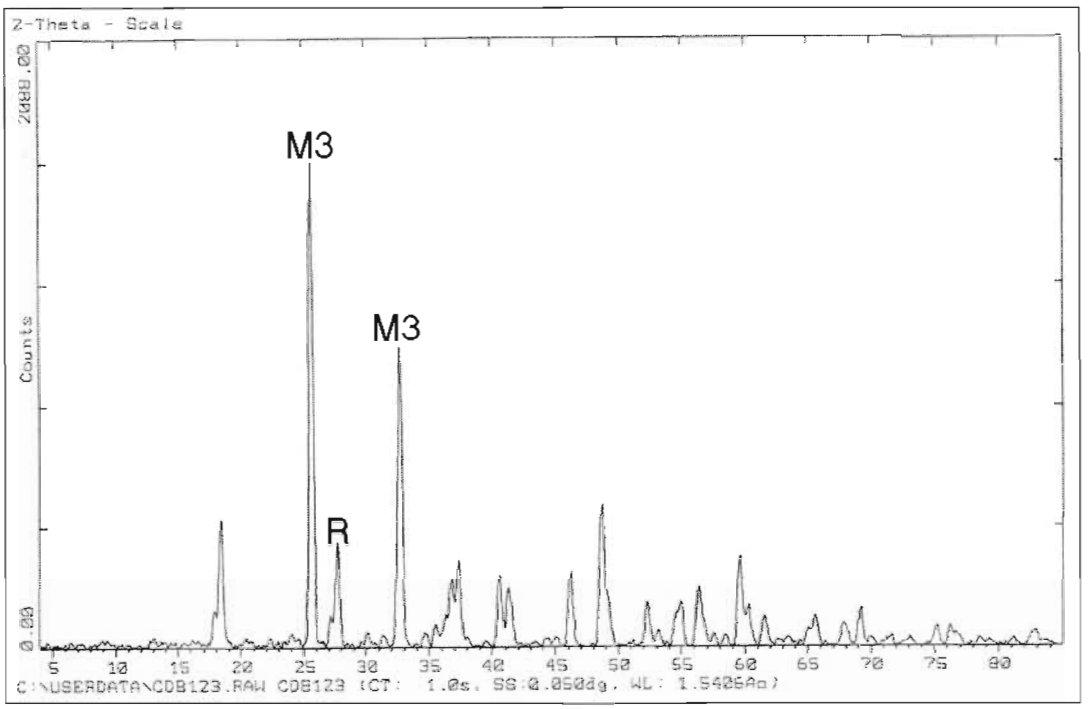
- Where the Mössbauer data is used, with both Fe^{2+} and Fe^{3+} present, chemical equilibrium has not been attained due to the co-existence of Fe^{3+} and Ti^{3+}.
- From these calculations it does seem that Ti^{3+} is still present in the samples.
- It seems that the error in the oxygen analysis will have the greatest impact on the calculation of the composition.

APPENDIX I: X-ray diffraction patterns for the miniature block samples

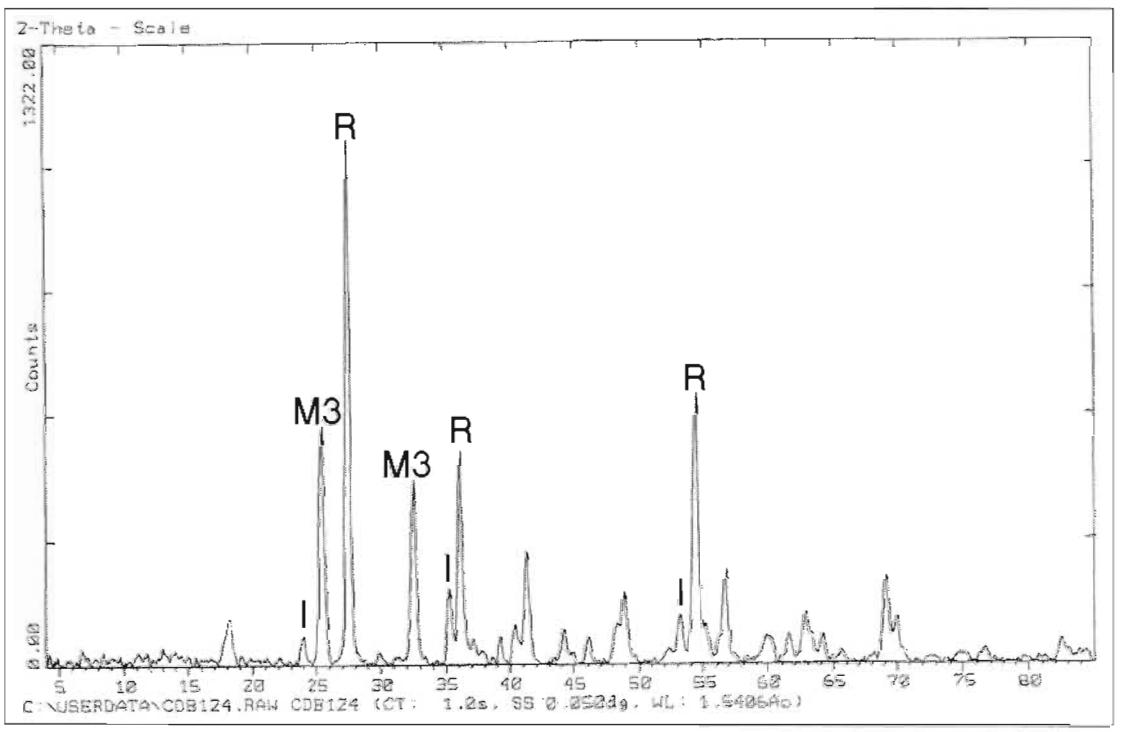
The following abbreviations are used for the identification of phases:

M3 – M_3O_5 phase	R – Rutile	I – Ilmenite
M6 – M_6O_{11} phase	A – Anatase	

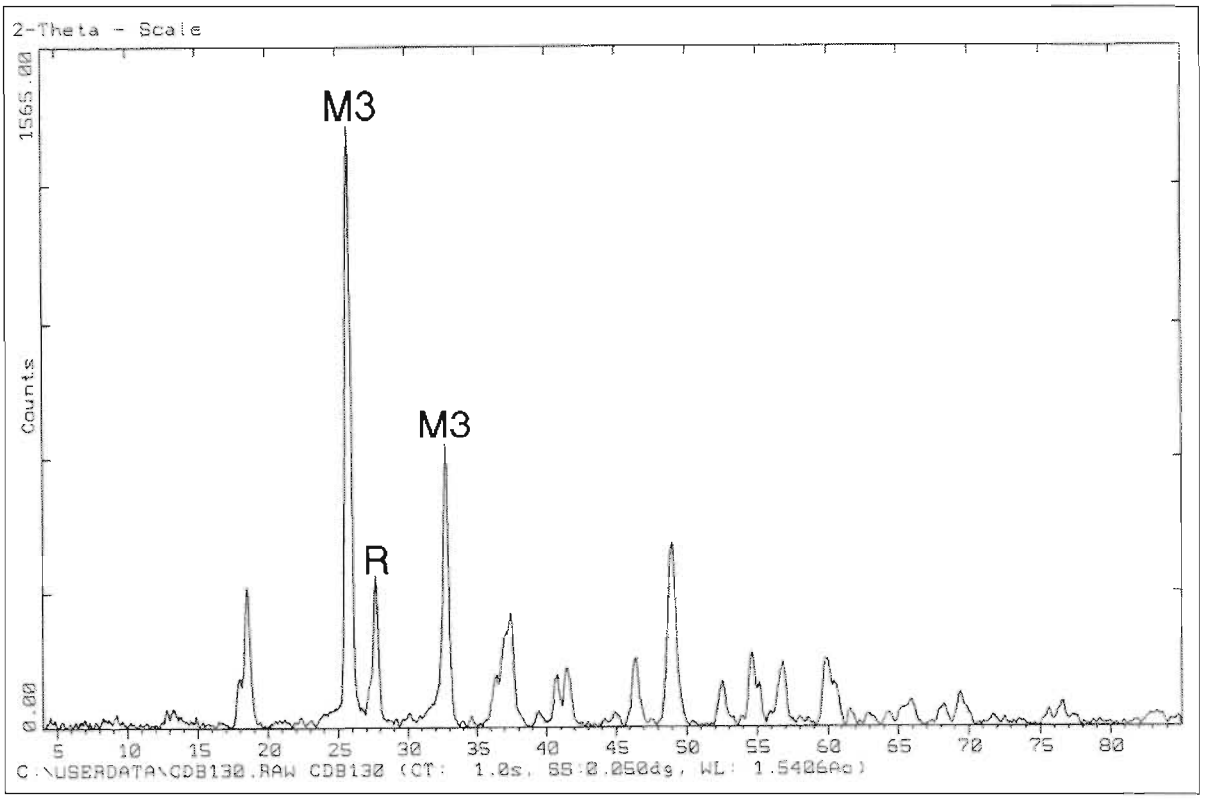
Sample DB123: Starting material for tests with pellets



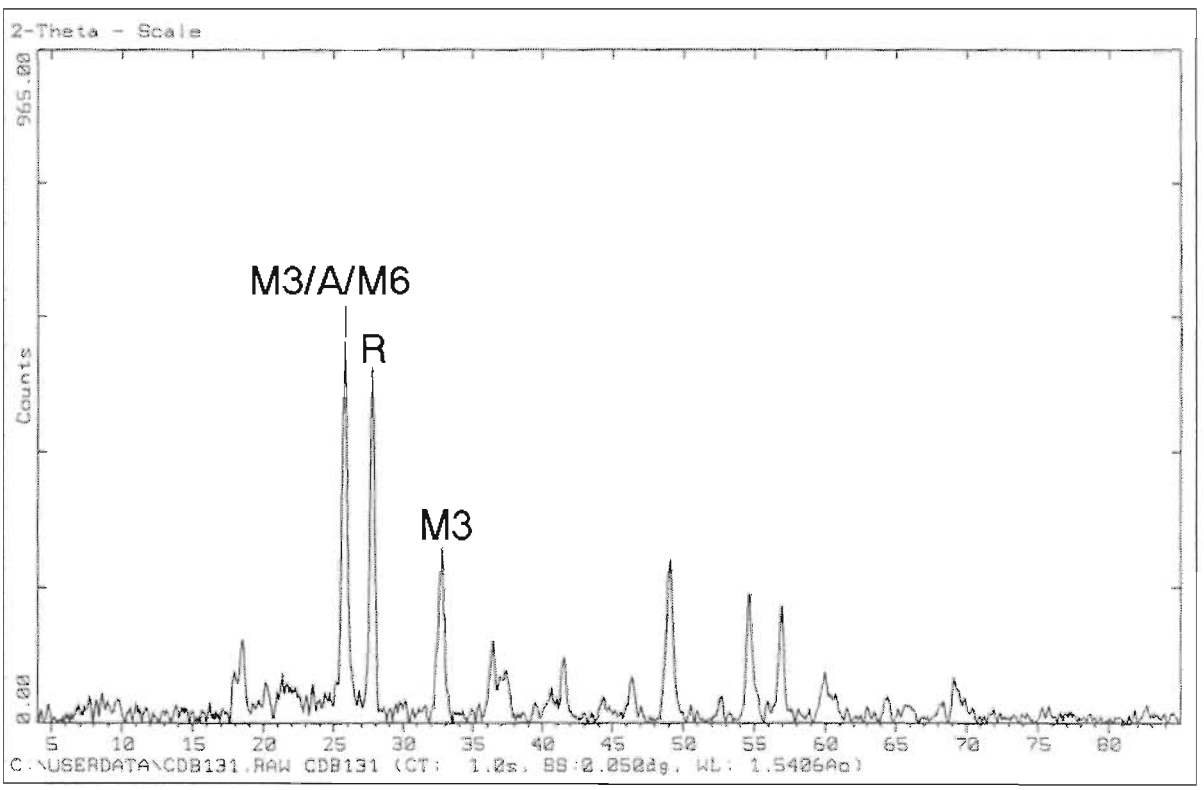
Sample DB124: Miniature Block; 800 °C; 24 hours



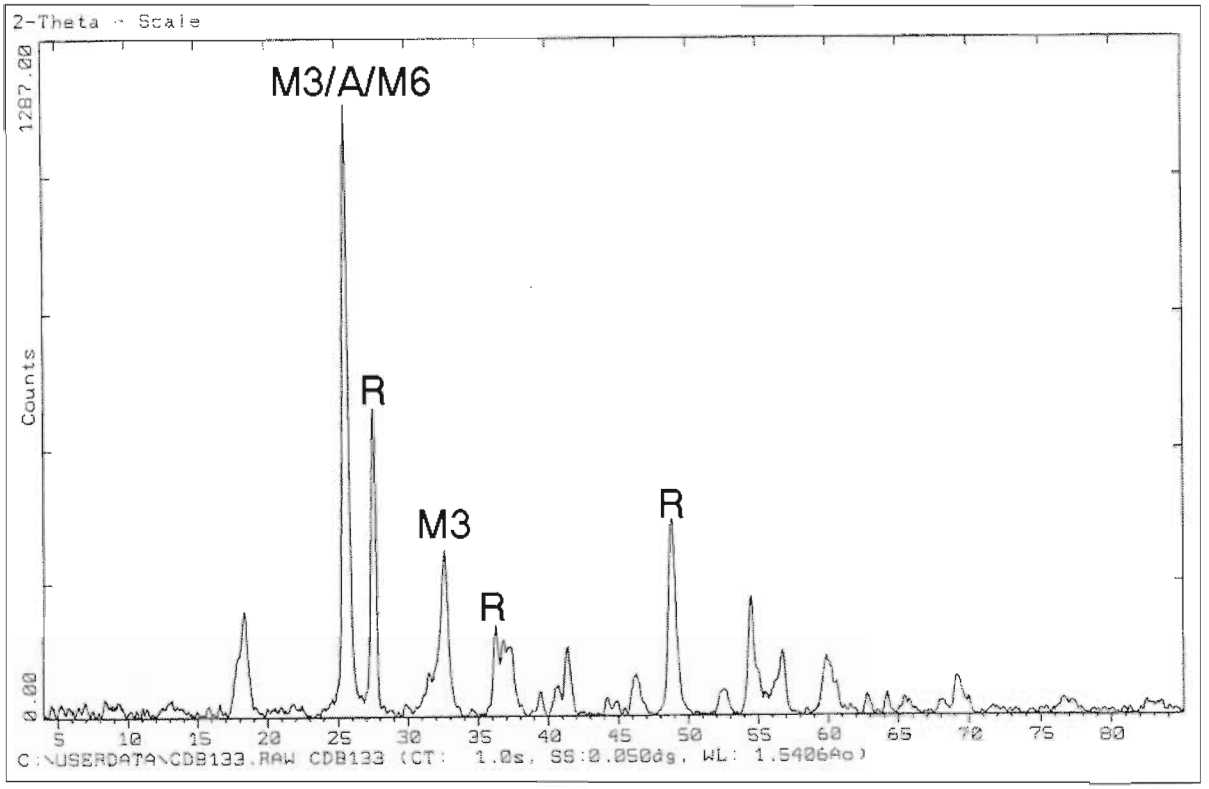
Sample DB130: Miniature Block; 400 °C; 6 hours



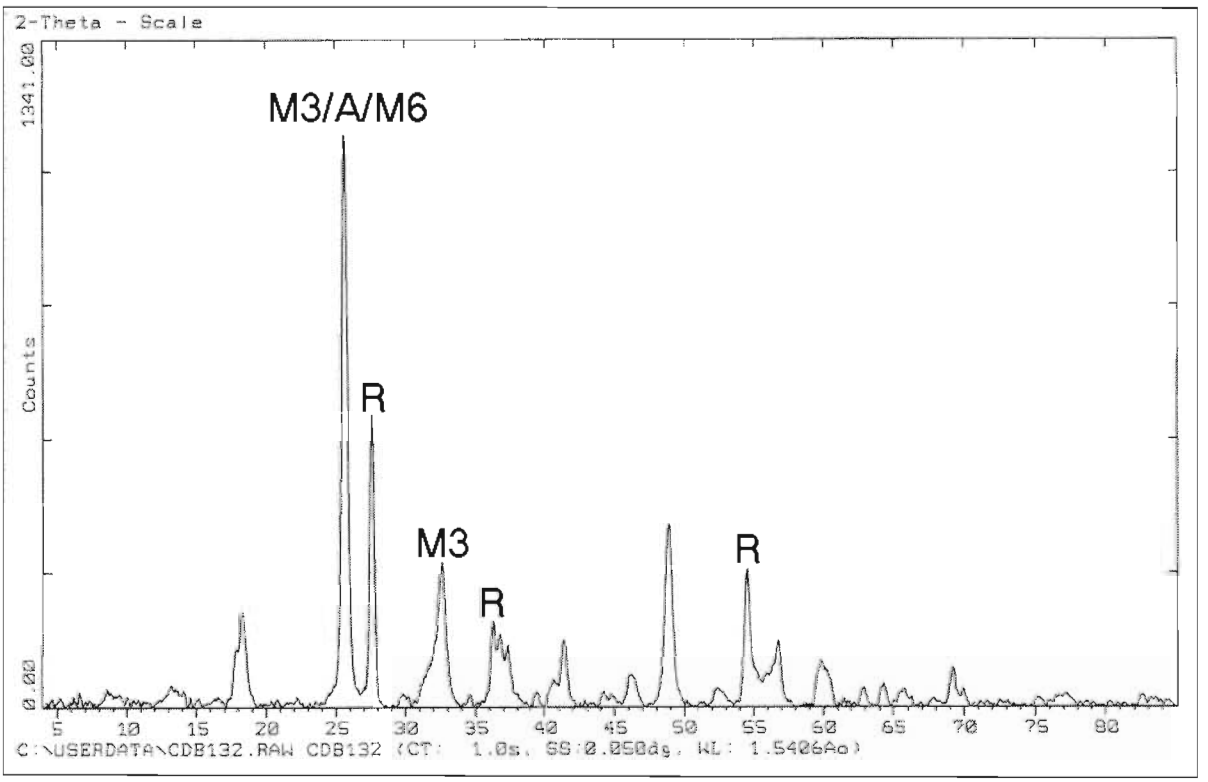
Sample DB131: Miniature Block; 400 °C; 24 hours



Sample DB133: Miniature Block; 400 °C; 96 hours



Sample DB132: Miniature Block; 400 °C; 384 hours



Appendix J: Statistical analyses of the data obtained from the crushing testwork on miniature slag blocks

1. Results for statistical analyses

The various results obtained from the crushing of the miniature slag blocks are given in Table 45 and Table 46. The integral area value in Table 45 was obtained by determing the area under the graph (Force as a function of time) obtained for each experiment (see Figure 55 for an example of such a graph). The slope values were obtained by determining the slope of the displacement as a function of time (see Figure 54 for an example). Calibration constants were used to convert the data to from volts to the required units. The total crushing energy was calculated as the product of the integral area and the slope value for each experiment. The absolute value was used, as the negative values are only a result of the reference point used for the displacement. The maximum force applied during the crushing of each miniature slag block is also shown in Table 45.

The sieve analyses of the miniature slag blocks after the completion of each experiment is shown in Table 46. It was decided to use the -500 μm sieve fraction to differentiate between the various experimental conditions.

2. Introduction to statistical analyses used

All the data generated for the various samples were subjected to the one-way analysis of variance (ANOVA) technique. This technique deals with the differences between sample means. The following two assumptions are made:
a) It is assumed that each set of data is normally distributed around the population mean.
b) It is assumed that each population of scores has the same variance.

The following calculations were made to compute the ANOVA summary tables (i; j - represents the various experimental groups):
$T_j = \Sigma X_j$ (X - data point)
$N = \Sigma n_j$ (n_j - number of data points in each experimental group)
$G = \Sigma X = \Sigma T_j$
$df_{Total} = N-1$
$df_{Group} = k-1$
$df_{Error} = df_{Total} - df_{Group}$
$SS_{Total} = \Sigma X^2 - G/N$ (SS – Sums of squares)
$SS_{Group} = \Sigma(T_j^2/n_j)$
$SS_{Error} = SS_{Total} - SS_{Group}$
$MS_{Group} = SS_{Group}/ df_{Group}$ (df – Degrees of freedom; MS – Mean squares [calculation of the variance])
$MS_{Error} = SS_{Error}/ df_{Error}$
$F = MS_{Group}/MS_{Error}$

Table 45: Results obtained from the crushing strength testwork

Test no.	Temperature of test (°C)	Duration of test (hours)	Maximum Force measured during crushing test (kN)	Average maximum force measured during crushing tests (kN)	Integral value (kN.s)	Slope value ($mm.s^{-1}$)	Total crushing energy – Absolute values (J)	Average crushing energy for each condition (J)	Standard deviation
Slag1	-	-	1.65	2.36	0.2923	-5.6036	1.6379	2.31	0.65
Slag2	-	-	3.29		0.5455	-5.4992	2.9998		
Slag3	-	-	2.24		0.4309	-6.3254	2.7256		
Slag4	-	-	2.25		0.2997	-6.3160	1.8929		
6241	600	24	4.70	4.71	0.9753	-5.2388	5.1094	6.26	2.46
6242	600	24	6.90		1.9217	-5.1199	9.8388		
6243	600	24	3.52		0.7031	-6.1462	4.3214		
6244	600	24	3.72		0.9085	-6.3483	5.7675		
6961	600	96	2.27	2.49	0.5395	-5.7561	3.1054	3.82	0.93
6962	600	96	2.43		0.6697	-5.5655	3.7272		
6963	600	96	2.01		0.5246	-6.2248	3.2655		
6964	600	96	3.23		0.8351	-6.1871	5.1668		
8241	800	24	8.66	6.87	24.9287	-2.1537	53.6891	22.65	20.71
8242	800	24	-		2.3781	-5.7333	13.6342		
8243	800	24	6.13		1.9484	-6.1132	11.9109		
8244	800	24	5.82		1.8427	-6.1744	11.3775		

Table 46: Sieve analyses of the slag after crushing

Test no.	Temperature of test (°C)	Duration of test (hours)	Sieve analysis of slag after crushing (mass %)					Average of the -500 µm sieve analyses (%)
			+1 mm	-1mm+500 µm	-500 µm+212 µm	-212 µm+75 µm	-75 µm	
Slag1	-	-	39.54	18.92	25.98	12.06	3.51	44.64
Slag2	-	-	40.34	17.27	25.05	13.80	3.54	
Slag3	-	-	29.39	17.03	30.72	18.92	3.93	
Slag4	-	-	40.31	18.64	25.00	13.17	2.88	
6241	600	24	48.43	23.78	17.62	7.58	2.59	28.40
6242	600	24	48.37	22.68	17.29	8.94	2.72	
6243	600	24	50.43	21.54	16.49	8.88	2.66	
6244	600	24	47.28	23.90	18.08	8.59	2.15	
6961	600	96	69.55	14.16	9.34	5.14	1.81	18.08
6962	600	96	73.66	12.36	8.12	4.32	1.54	
6963	600	96	70.36	15.57	7.69	5.25	1.13	
6964	600	96	54.12	17.91	15.09	9.05	3.82	
8241	800	24	61.27	18.47	10.78	6.29	3.19	20.67
8242	800	24	63.42	16.30	10.67	5.93	3.68	
8243	800	24	57.39	18.46	14.03	6.44	3.68	
8244	800	24	66.74	15.26	9.94	5.44	2.62	

For the purpose of the calculations the following nomenclature was used:
1: Untreated slag
2: Slag treated at 600 °C for 24 hours
3: Slag treated at 600 °C for 96 hours
4: Slag treated at 800 °C for 24 hours

The following null hypothesis were made for each scenario:

$$H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$$

In each instance the null hypothesis was rejected. Because of this the protected t test (also known as Fisher's least significant difference test) was used to investigate hypotheses involving means of individual groups.

The following equation (for comparing two means) was used to calculate t (using the means of each group and the number of data points in each group):

$$t = \frac{\overline{X_i} - \overline{X_j}}{\sqrt{MSError(\frac{1}{ni} + \frac{1}{nj})}}$$

Details of the statistical techniques used are given extensively by Howell.

3. Statistical analyses of the total energy required for crushing

The total crushing energy required for crushing the miniature slag blocks were compared on the basis of the experimental treatment of the respective slag blocks. The ANOVA summary for the total crushing energy is given in Table 47. As F is less than the critical F statistic ($F_{calculated} = 3.24 < F_{0.05;3;12} = 3.49$), we must accept H_0 at the level of $\alpha = 0.05$. This implies that there are no significant differences between the means of the various experimental groups.

If we however relax the conditions to $\alpha = 0.10$, $F_{0.10;3;12}$ is calculated to be 2.61. We therefore expect to exceed a F of 2.61 only 10 per cent of the time if H_0 were true. Under these conditions we can reject H_0 and use the protected t test to distinguish between the means of the various experimental groups.

Table 47: ANOVA summary of total energy required for the crushing of miniature slag blocks

Source	Df	SS	MS	F
Groups	3	1061.03	353.68	3.24
Error	12	1309.15	109.10	
Total	15	2370.18		

The critical t statistic (two tailed) used for the protected t test is $t_{0.10;12} = \pm 1.782$. The results obtained from comparing the various means are shown in Table 48. The table shows that only

the mean of the slag treated at 800 °C is significantly different to the means of the other slag samples (where H_0 is rejected). No significant differences were observed between the mean of the untreated slag samples and the means of the samples treated at 600 °C. These insensitive results are mainly due to the high value of 109.1 calculated for MS_{Error}.

Table 48: Summary of the results for the protected t test for the total energy required for crushing the miniature slag blocks

H_0	t	Result
$\mu_1 = \mu_2$	-0.53	Accept H_0
$\mu_1 = \mu_3$	-0.20	Accept H_0
$\mu_1 = \mu_4$	-2.75	Reject H_0
$\mu_2 = \mu_3$	0.33	Accept H_0
$\mu_2 = \mu_4$	-2.22	Reject H_0
$\mu_3 = \mu_4$	-2.55	Reject H_0

4. Statistical analysis of the maximum force measured during crushing

The maximum force measured during crushing of the miniature slag blocks were compared on the basis of the experimental treatment of the respective slag blocks. The ANOVA summary for the maximum force measured during crushing is given in Table 49. As F is greater than the critical F statistic ($F_{calculated} = 11.97 > F_{0.05;3;11} = 3.59$), we can therefore reject H_0. As we reject H_0, we can use the protected t test to distinguish between the means of the various experimental groups.

Table 49: ANOVA summary of maximum force required for crushing of miniature slag blocks

Source	df	SS	MS	F
Groups	3	46.61	15.54	11.97
Error	11	14.27	1.30	
Total	14	60.88		

The critical t statistic (two tailed) used for the protected t test is $t_{0.05;11} = \pm 2.201$. The results for the comparison of the various means are shown in Table 50.

Table 50: Summary of the results for the protected t test for the maximum force measured during crushing of the miniature slag blocks

H_0	**t**	**Result**
$\mu_1 = \mu_2$	-2.92	Reject H_0
$\mu_1 = \mu_3$	-0.16	Accept H_0
$\mu_1 = \mu_4$	-5.19	Reject H_0
$\mu_2 = \mu_3$	2.76	Reject H_0
$\mu_2 = \mu_4$	-2.48	Reject H_0
$\mu_3 = \mu_4$	-5.04	Reject H_0

The table shows that only the following set of means is not significantly different:

- Between the untreated slag and the slag treated at 600 °C for 96 hours.

5. Statistical analysis of the sieve analyses of the slag after crushing

The -500 µm sieve fractions of the samples obtained after the crushing of the miniature slag blocks were compared on the basis of the experimental treatment of the respective slag blocks. The ANOVA summary for this comparison is shown in Table 51. As F is greater than the critical F statistic ($F_{calculated} = 26.23 > F_{0.05;3;11} = 3.49$), we can therefore reject H_0. As we reject H_0, we can use the protected t test to distinguish between the means of the various experimental groups.

Table 51: ANOVA summary of percentage slag less than 500 µm after crushing

Source	Df	SS	MS	F
Groups	3	1716.60	572.20	26.23
Error	12	261.74	21.81	
Total	15	1978.34		

The critical t statistic (two tailed) used for the protected t test is $t_{0.05;12} = \pm 2.179$. The results for the comparison of the various means are shown in Table 52. The table shows that only the following set of means is not significantly different:

- Between the slag treated at 600 °C for 96 hours and the slag treated at 800 °C for 24 hours.

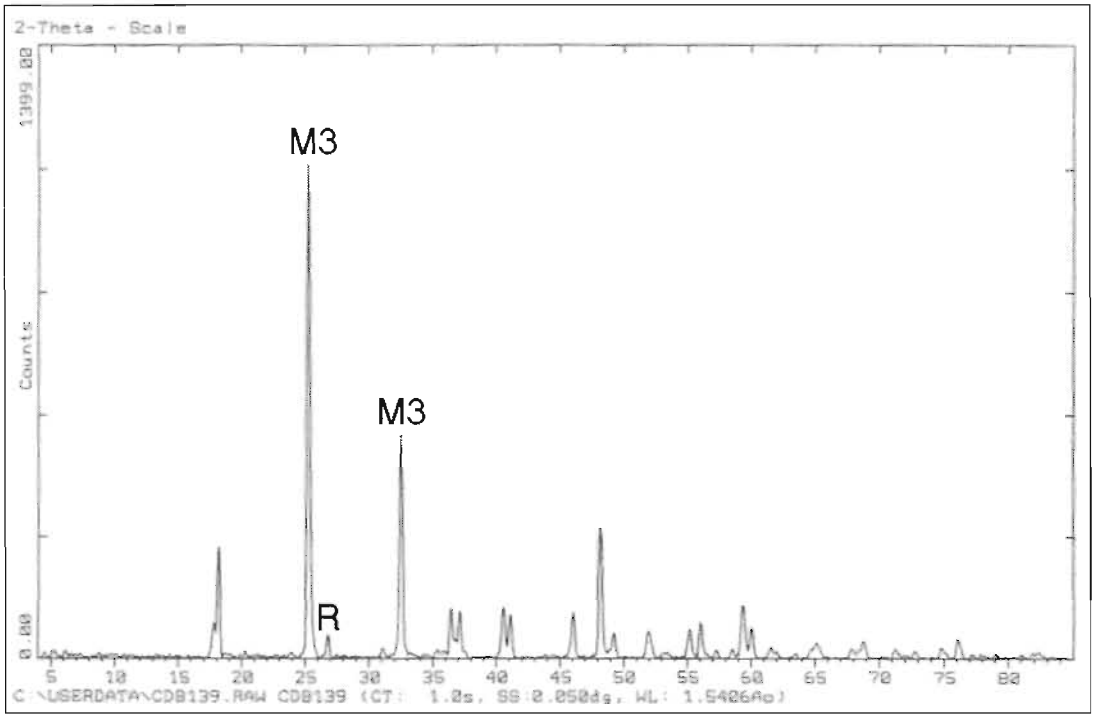
Table 52: Summary of the results for the protected t test for the percentage of slag less than 500 µm after crushing

H_0	t	Result
$\mu_1 = \mu_2$	4.92	Reject H_0
$\mu_1 = \mu_3$	8.04	Reject H_0
$\mu_1 = \mu_4$	7.26	Reject H_0
$\mu_2 = \mu_3$	3.12	Reject H_0
$\mu_2 = \mu_4$	2.34	Reject H_0
$\mu_3 = \mu_4$	-0.79	Accept H_0

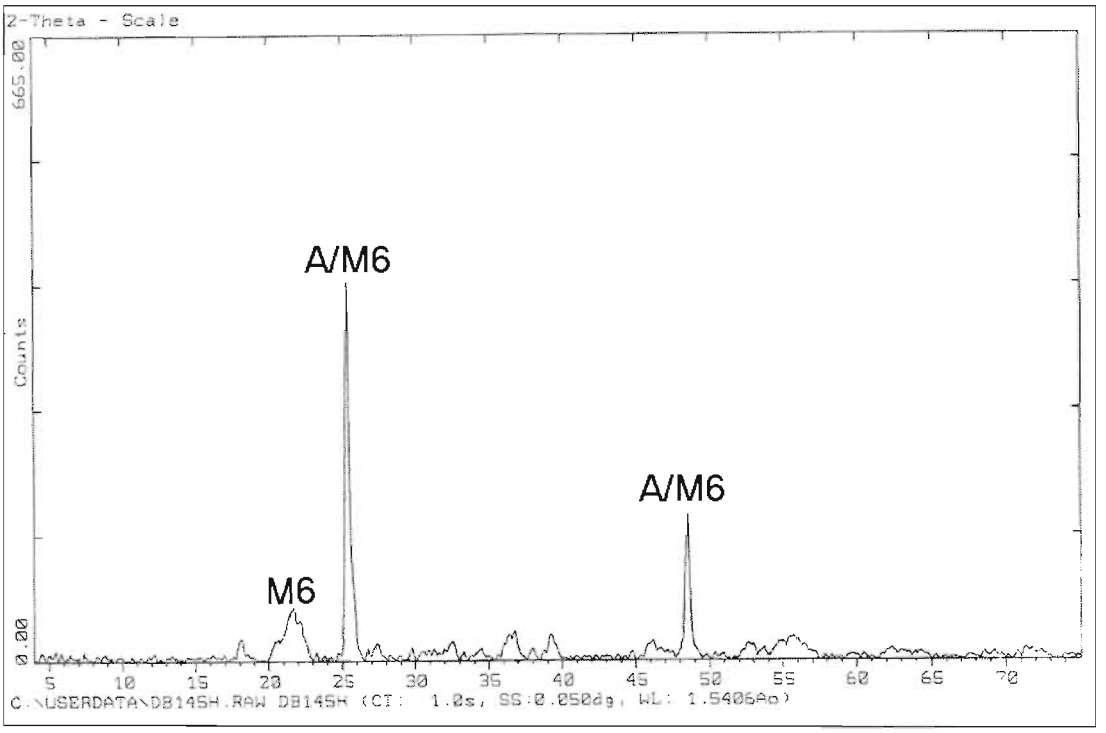
APPENDIX K: X-ray diffraction patterns of samples used in unidirectional crushing testwork

The following abbreviations are used for the identification of phases:
M3 – M_3O_5 phase R – Rutile M6 – M_6O_{11} phase A – Anatase

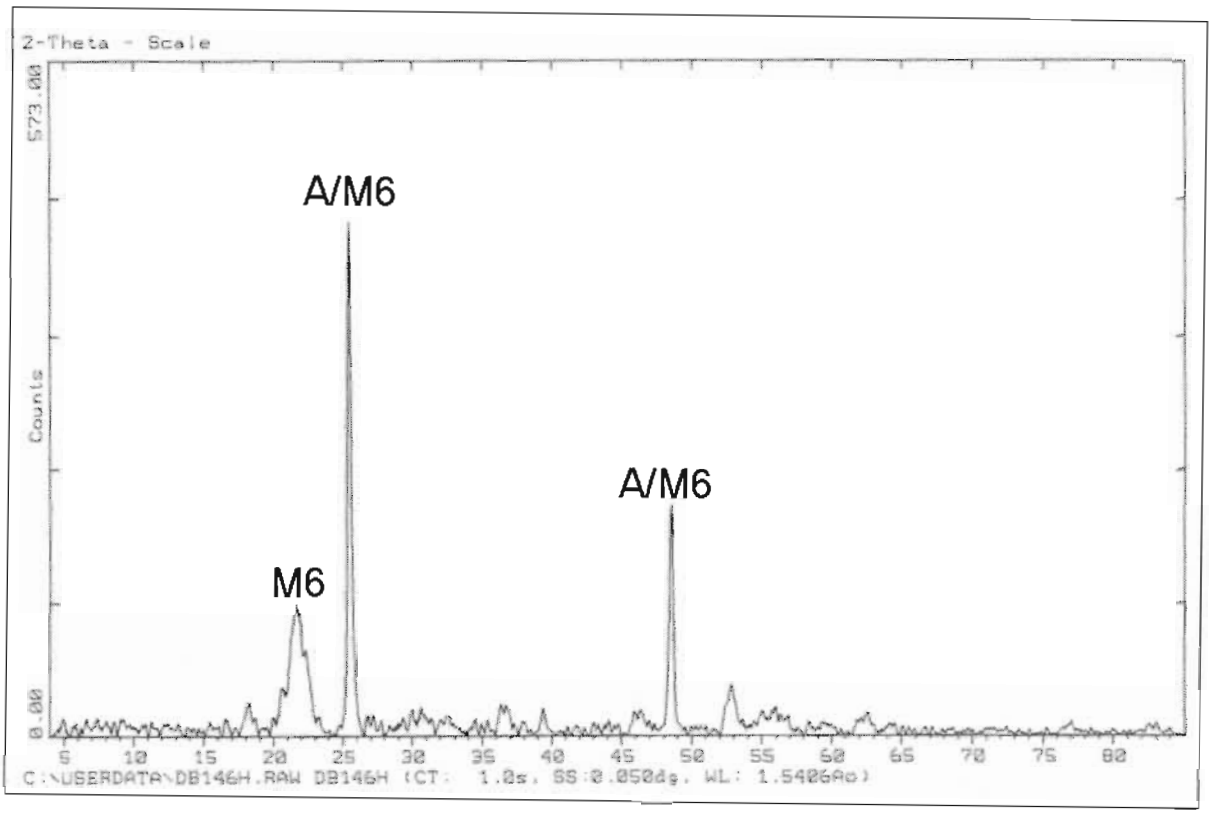
Sample DB139: Untreated sample (Slag 2), -212 µm fraction



Sample DB145: Sample treated for 24 hours at 400 °C (-1 mm fraction obtained after decrepitation on quenching)



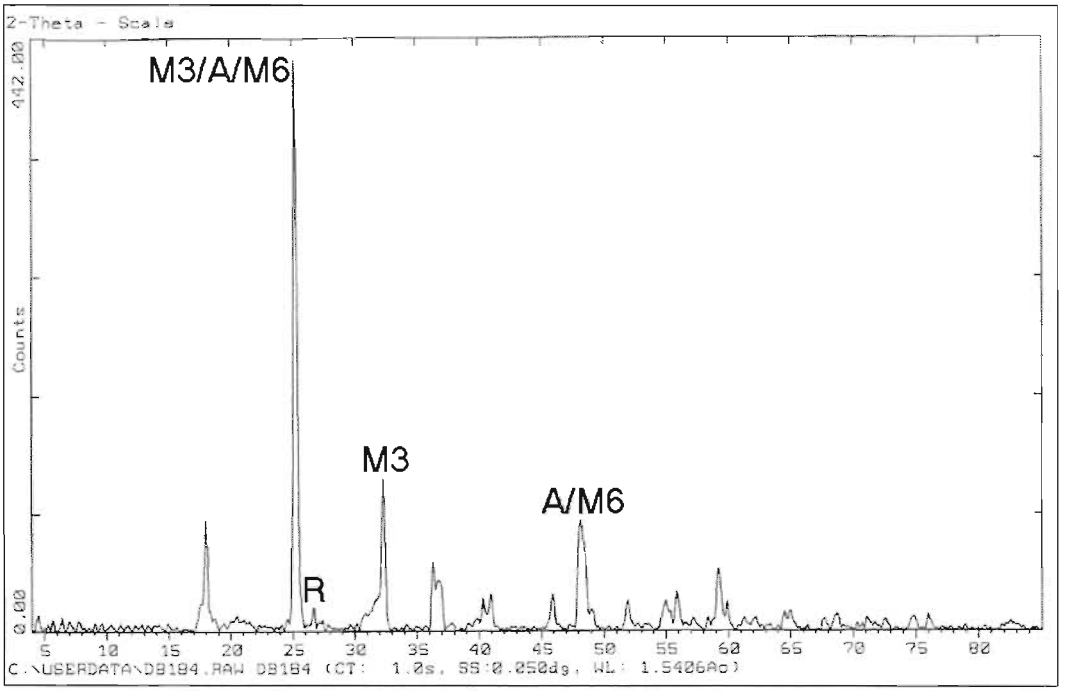
Sample DB146: Sample treated for 24 hours at 400 °C (+1 mm fraction obtained after decrepitation on quenching)



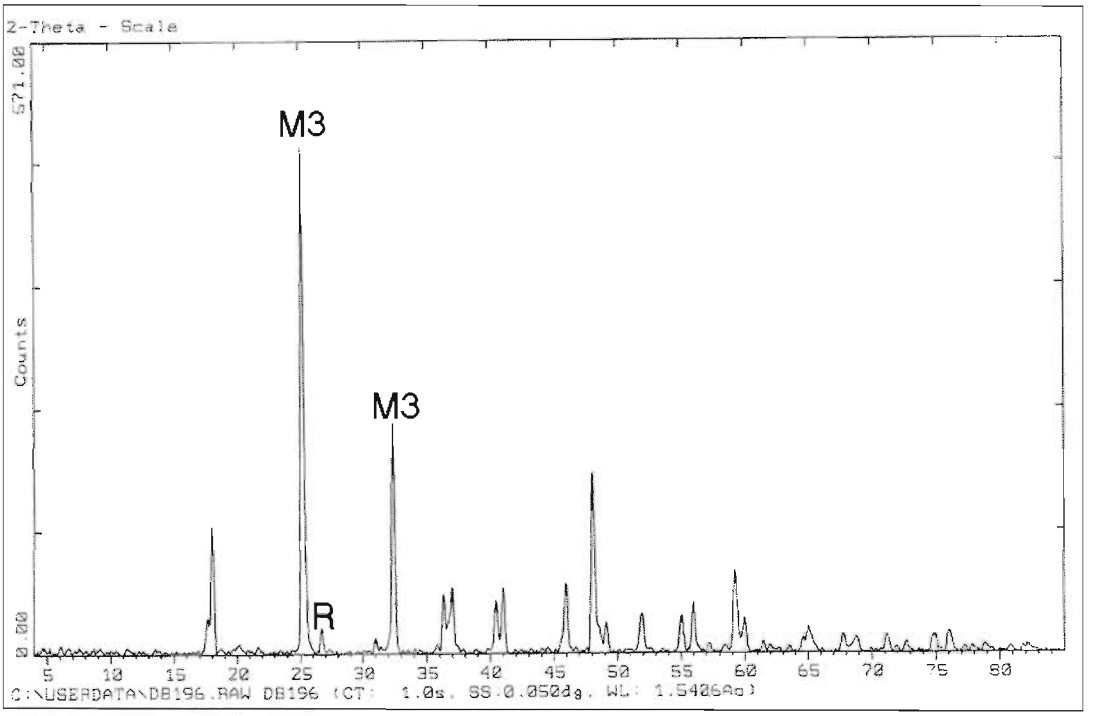
APPENDIX L: X-ray diffraction patterns of samples treated in different atmospheres

The following abbreviations are used for the identification of phases:
M3 – M_3O_5 phase R – Rutile M6 – M_6O_{11} phase A – Anatase

Sample DB184: Powder sample treated in air for 24 hours at 400 °C (Starting material DB100)



Sample DB196: Powder sample treated in argon for 24 hours at 400 °C (Starting material DB100)



Appendix M: Investigation into the interaction between the SiC sheath material and titania slag

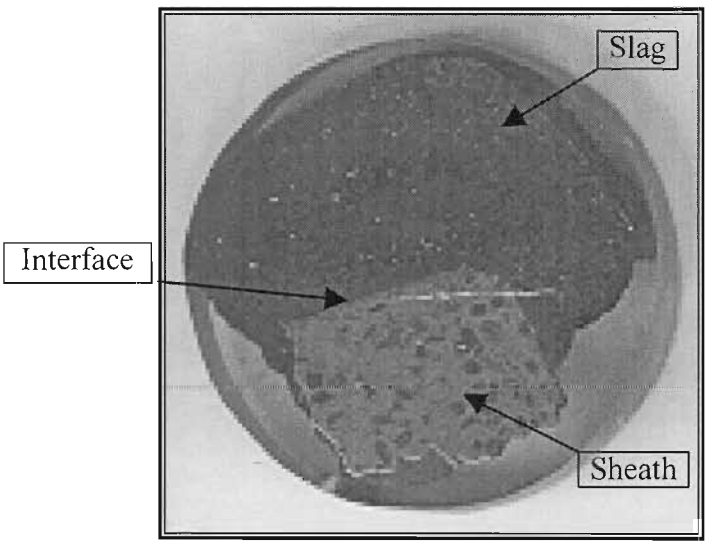
1. Introduction

For the determination of the cooling rate of the slag blocks during the 3MVA smelting campaign a thermocouple configuration was used with SiC as the outer sheath. At the completion of the cooling tests the sheath material was recovered to investigate whether any chemical reaction had taken place between the SiC sheath material and the titania slag. The SiC sheath material was in direct contact with the titania slag over a period of several days. The results obtained from the sheath used in tap 73 are given below. Over the test period a maximum temperature of 1654 °C was measured by the thermocouple (see Figure 61 for data on the cooling of the slag blocks).

2. Results

Figure 67 shows a photograph of the polished block prepared from a piece of the SiC sheath material contained in the slag. The interface between the sheath material and the titania slag appears to be well defined and relatively sharp. Some material from the slag/sheath interface were analysed by X-ray diffraction showing the following results:
Main phase – M_3O_5
Minor phase – Silicon carbide
Trace – Rutile.

Figure 67: Photograph of the polished block prepared from a piece of the sheath material embedded in the slag



The sheath material consists of coarse-grained SiC particles contained in a fine SiC matrix. The sheath material seems to be slightly porous. This can be seen in Figure 68. In Figure 69 a photograph of the sheath/slag interface is shown. In the top right of the photograph the SiC sheath can be observed, while in the bottom left the titania slag can be seen. In-between a reaction zone, approximately 250 μm in width can be observed. This interface is characterised

by the presence of SiC particles, a ferro-silicon phase (containing trace amounts of titanium), titanium oxide rich slag and a silicon oxide rich glass phase. Trace amounts of fine-grained titanium carbide were also observed to be present in some areas of the interface (not shown in the figures).

Figure 68: Micrograph of the SiC sheath material (back-scattered electron image)

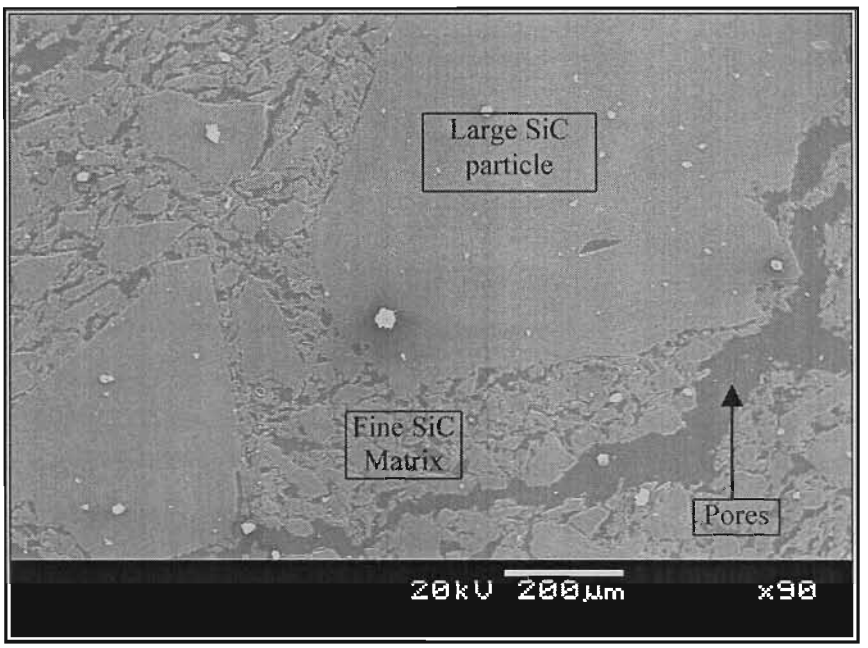
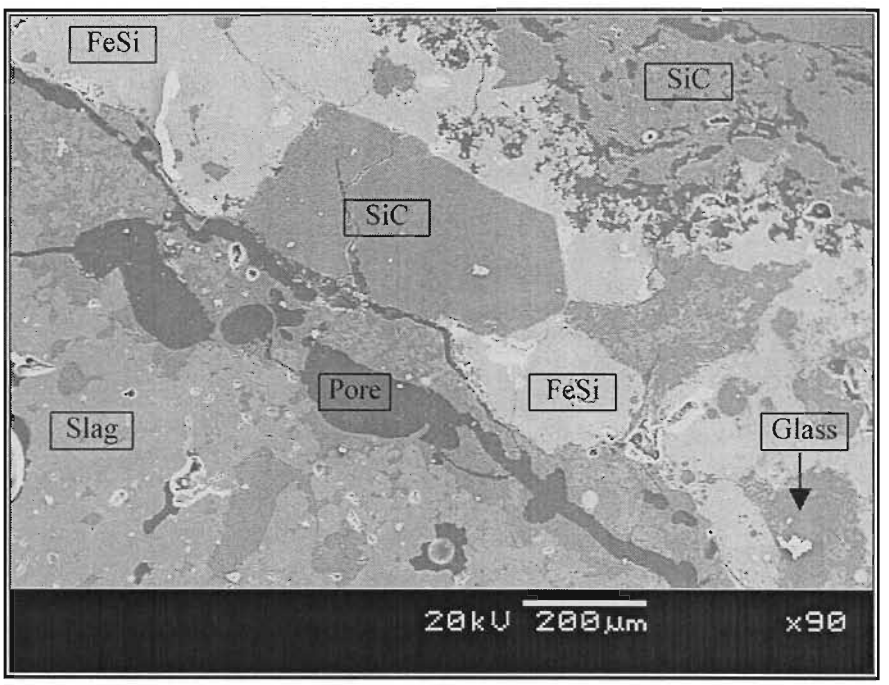


Figure 69: Micrograph of the sheath/slag interface



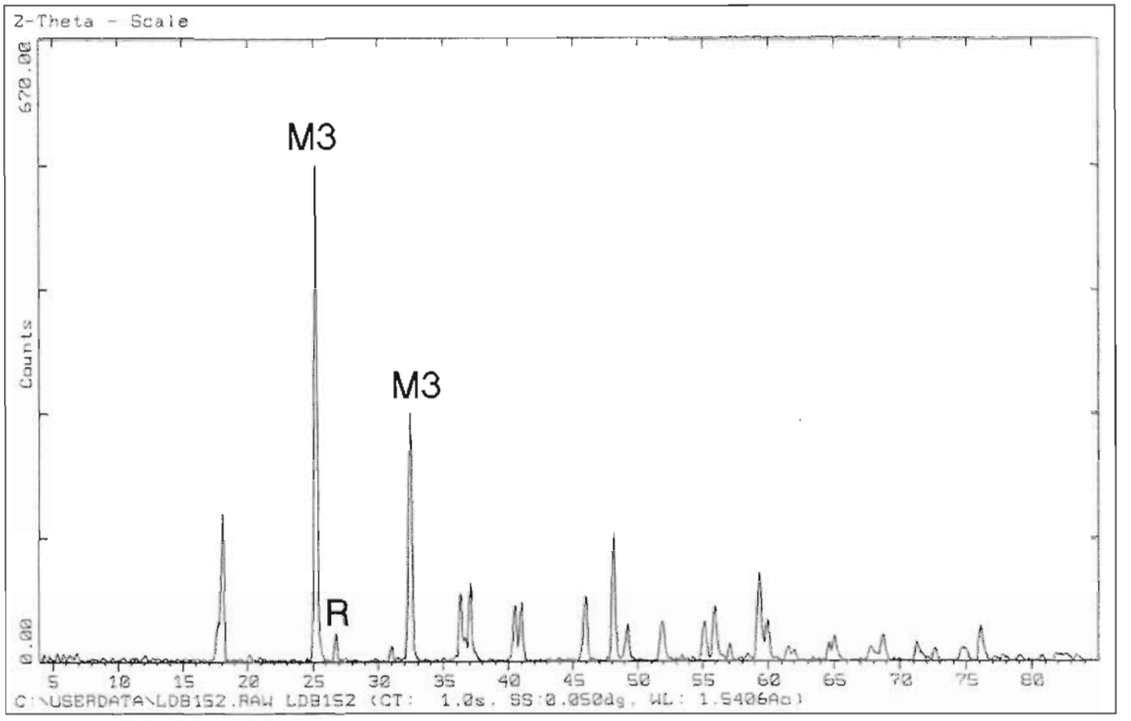
3. Conclusions

The SiC sheaths maintained their integrity and no catastrophic failure of the two sheaths occurred. From these results it seems that some chemical reactions took place at the interface between the slag and the sheath. This was however restricted to a small zone of approximately 250 μm. It seem that the M_3O_5 slag reacted with the SiC in the sheath to form ferro-silicon and silica rich glass phases, with some traces of TiC also present. The compositions of these phases were not investigated. It can be recommended that the SiC sheath material be used again for future testwork of this nature.

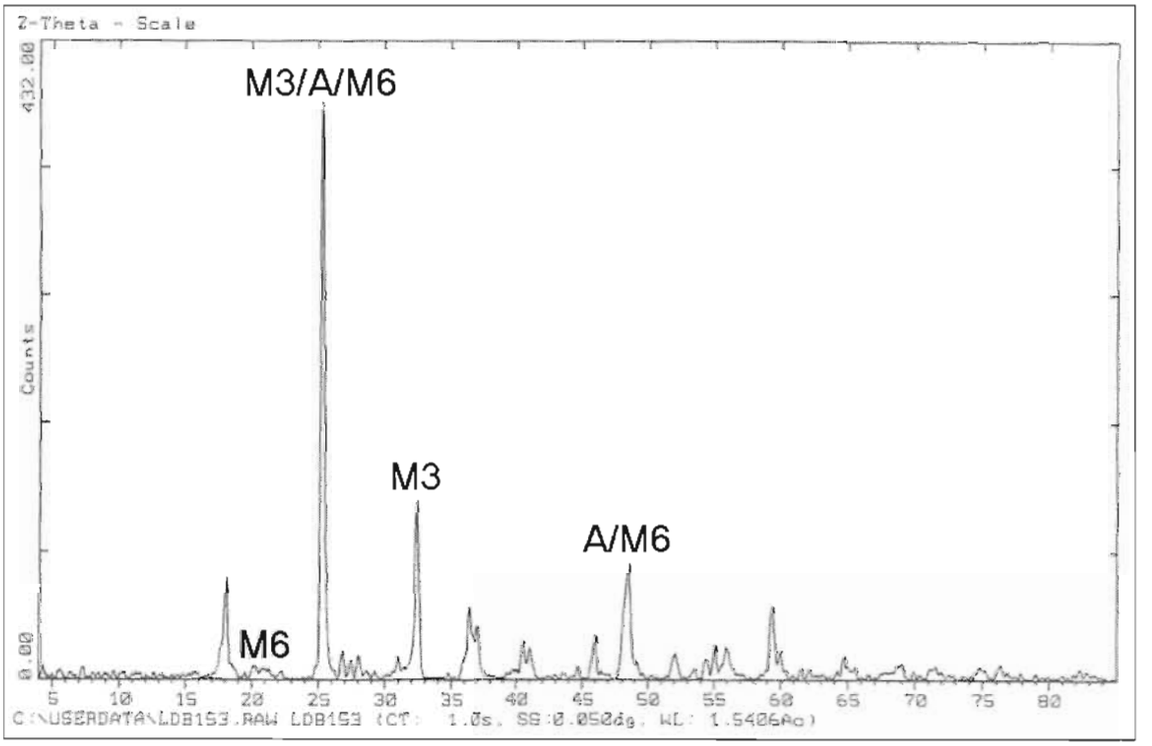
APPENDIX N: X-ray diffraction patterns for the decrepitated slag samples obtained during the ilmenite smelting campaign

The following abbreviations are used for the identification of phases:
M3 – M_3O_5 phase R – Rutile M6 – M_6O_{11} phase A – Anatase

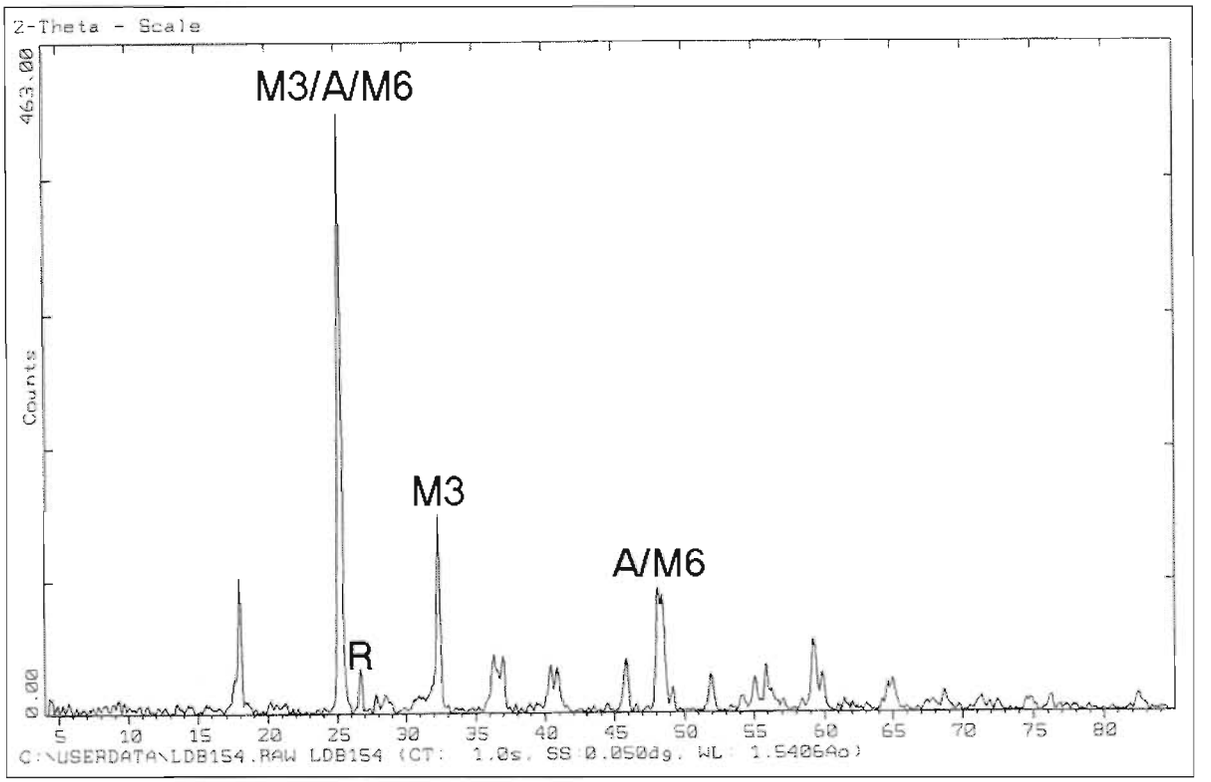
Sample DB152: Starting material obtained from tap stream (tap 68)



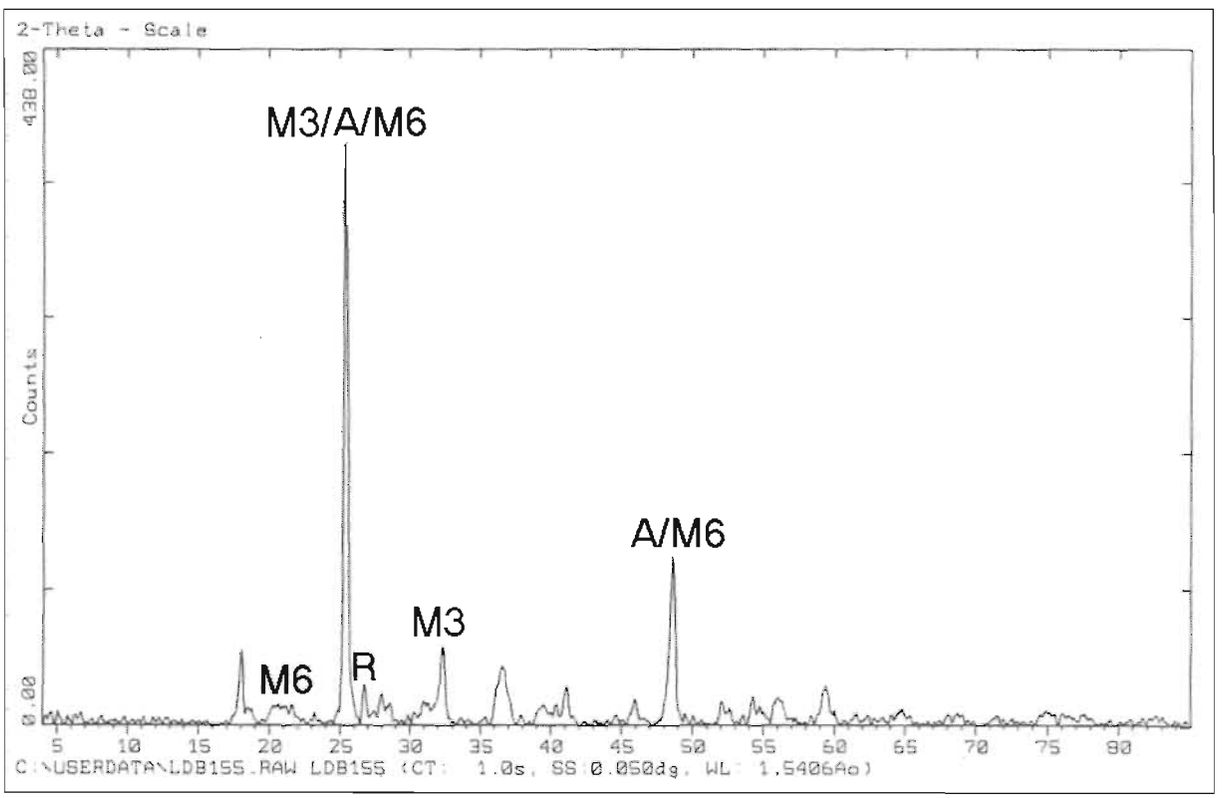
Sample DB153: Decrepitated sample from tap 68



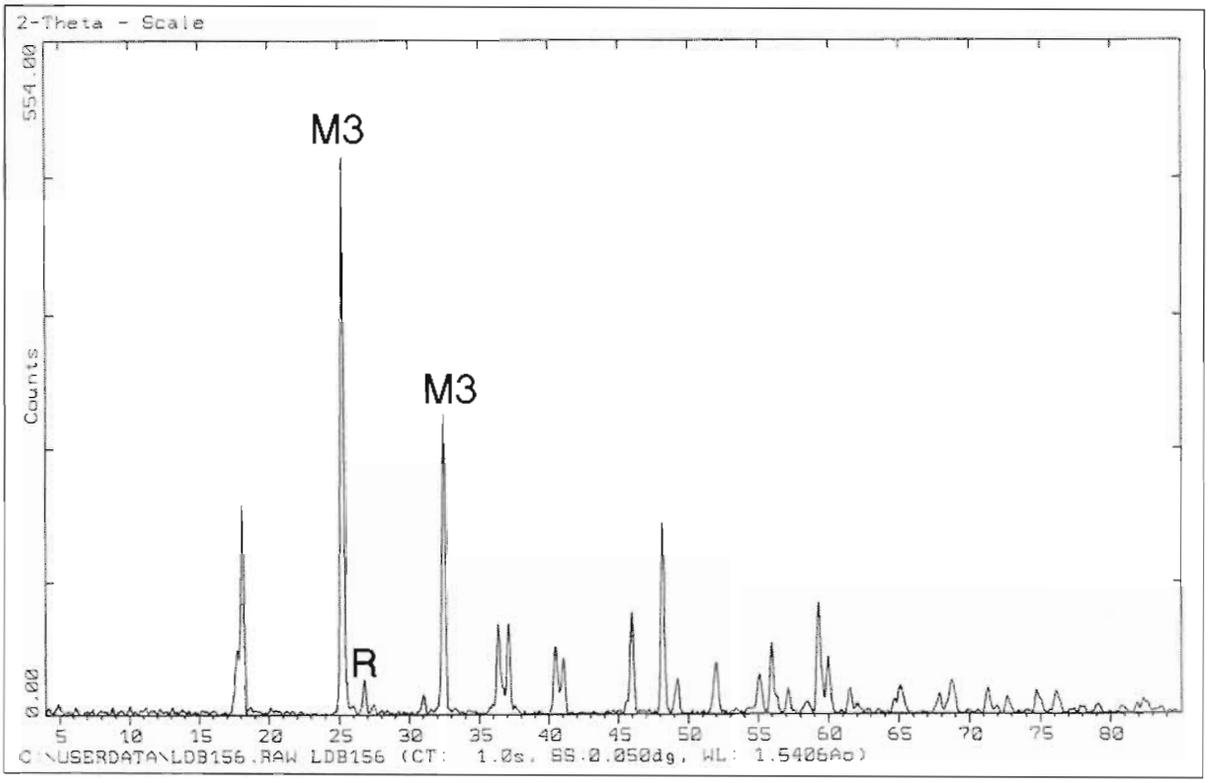
Sample DB154: Decrepitated sample from tap 68



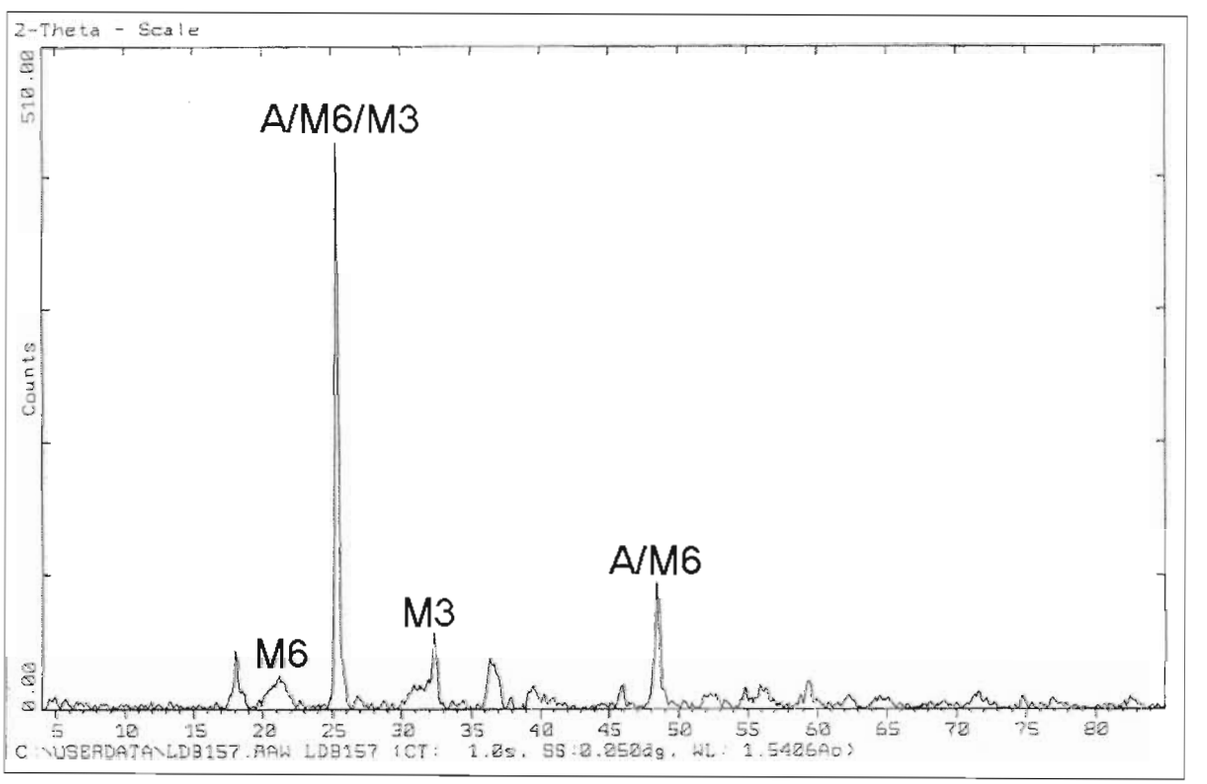
Sample DB155: Decrepitated sample from tap 68



Sample DB156: Starting material obtained from tap stream (tap 70)



Sample DB157: Decrepitated sample from tap 70



Appendix O: Data from density measurements

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Private Bag X3015Randburg 2125, South Africa

In your Reply please quote: 4189801

Mr Deon Bessinger
Iscor R&D
P.O. Box 450
Pretoria
South Africa
0001

Dear Deon

Density Measurements

I have pleasure in presenting you with our results of the density measurements for the six samples submitted.

The samples were pulverised in a rotating disc mill for 60 seconds to equalise their particle size distributions. The samples were dried overnight at 140°C to remove moisture, and cooled under vacuum to degas the surfaces of the particles and minimise surface porosity effects. A known mass (approximately 16g if available) of material was placed in a helium stereopychnometer and purged for 10 cycles before the volume of the samples was measured at ambient temperature. Ten volume measurements were made per sample and the results averaged. The density was calculated from the volume measurement and sample mass (Table 1). Prior to making the measurements, the instrument was calibrated using a standard of known volume. The uncertainty in the precision of the measurement is also shown in Table 1 and was estimated by taking into account reproducibility, sample mass, temperature fluctuations and particle size distribution. Samples DB 152 and 155 have relatively large errors because the measurements were made using a relatively small sample mass in comparison to the other measurements.

Table 1. Density (g/cm^3 or equivalent units)

	DB 152	DB 155	DB 156	DB 157	DB 175	DB 178
1	3.9540	3.9434	3.9676	3.9400	3.9404	3.9285
2	3.9547	3.9429	3.9676	3.9397	3.9406	3.9288
3	3.9556	3.9442	3.9678	3.9406	3.9410	3.9282
4	3.9550	3.9435	3.9679	3.9397	3.9409	3.9279
5	3.9553	3.9421	3.9676	3.9394	3.9398	3.9272
6	3.9551	3.9441	3.9672	3.9404	3.9403	3.9263
7	3.9545	3.9433	3.9666	3.9392	3.9404	3.9261
8	3.9545	3.9439	3.9661	3.9395	3.9402	3.9252
9	3.9542	3.9413	3.9661	3.9391	3.9402	3.9241
10	3.9533	3.9431	3.9656	3.9390	3.9392	3.9240
Mean	3.9546	3.9432	3.9670	3.9397	3.9403	3.9266
Stdev	0.0007	0.0009	0.0008	0.0005	0.0005	0.0018
Uncertainty	0.028	0.092	0.028	0.047	0.028	0.028

Please feel free to contact me if you want to discuss the result in more detail.
Yours sincerely

Steve McCullough
MINERALOGY