

Partitioning of platinum-group

elements between metal and sulphide melt

in the Cu-S and Ni-S systems.

by

Henriëtte Ueckermann

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Applied Mineralogy at the Faculty of Natural Sciences and Engineering University of Pretoria Study leader: Prof. R.K.W. Merkle

February 2002



CONTENTS

List of Tables	viii
List of Figures	xiii
List of Abbreviations and Symbols	xviii
List of Mineral Formulae	xix
1. INTRODUCTION AND AIM OF STUDY	1
1.1. Choice of PGE contents for investigation	2
1.2. Choice of major element compositions of experiments	4
1.2.1. THE NI-S SYSTEM AT LOW S CONTENTS	4
1.2.2. THE CU-S SYSTEM AT LOW S CONTENTS	5
1.2.3. THE FE-S SYSTEM AT LOW S CONTENTS	5
1.3. Previous investigations of PGE partition coefficients	5
1.3.1. THE NI-S SYSTEM	5
1.3.2. THE CU-S SYSTEM	6
1,3.3. THE FE-S SYSTEM	6
1.3.4. THE FE-NI-S SYSTEM	7
1.3.5. THE CU-FE-NI-S SYSTEM	8
1.3.6. OTHER RELEVANT SYSTEMS	9
1.3.6.1. Pd-Fe-S system	. 9
1.3.6.2. Pt-Fe-S system	9 .
1.3.6.3. Rh-Fe-S system	9
1.3.6.4. Pd-Ni-S system	. 10
1.3.6.5. Cu-Pd-S system	10
1.3.6.6. Cu-Rh-S system	. 10
1.3.6.7. Fe-Ni-PGE systems	. 10
1.3.6.8. Fe-Ni-PGE-S system	11



2. EXPERIMENTAL TECHNIQUE	2
2.1. Sealed quartz glass tube technique	
2.2. Starting material 13	
2.3. Equilibration of experiments	
2.3.1. PRE-REACTION	
2.3.2. EQUILIBRATION	
2.3.3. QUENCHING	
2.4. Preparation of experiments for further investigation 18	
3. MICROSCOPICAL OBSERVATIONS	0
3.1. Optical properties of quenched phases	
3.1.1. NI-S SYSTEM	
3.1.1.1. Nickel	
3.1.1.2. Ni-S melt	
3.1.2. CU-S SYSTEM	
3.1.2.1. Copper	
3.1.2.2. Digenite (CuS)	
3.1.2.3. Cu-S melt	
3.1.3. FE-S SYSTEM	
3.1.3.1. Iron	
3.1.3.2. Troilite (FeS) and pyrrhotite (FeS _{1+x})	
3.1.3.3. Fe-S melt	
3.2. Textures	
3.2.1. NI-S SYSTEM	
3.2.1.1. Nickel - sulphide melt assemblage	
3.2.2. CU-S SYSTEM	
3.2.2.1. Copper - digenite assemblage	
3.2.2.2. Cu melt - digenite assemblage 31	
3.2.2.3. Cu melt - sulphide melt assemblage	
3.2.2.4. Digenite - sulphide melt assemblage	



3.2.3. FE-S SYSTEM	5
3.2.3.1. Iron - sulphide melt assemblage 36	5
3.2.3.2. Pyrrhotite - sulphide melt assemblage	5
3.2.3.3. Iron - troilite assemblage)

4.1,	Electron Probe Micro Analysis (EPMA)	40
4.2.	Particle Induced X-ray Emission (PIXE) Analysis	41
	4.2.1. MILLI-PIXE	43
	4.2.1.1. Evaluation of analytical conditions	47
	4.2.2. MICRO-PIXE	53
4.3.	Statistics	54
	4.3.1. RESAMPLING	55

5.1.	The Ni-S system	57
	5.1.1. NICKEL – NI-S MELT ASSEMBLAGE (1100°C - 700°C)	57
	5.1.1.1. EPMA results	57
	5.1.1.1.1. Separated drops	58
	5.1.1.2. PIXE results	62
	5.1.1.2.1. Milli-PIXE	62
	5.1.1.2.1.1. Results for equilibration at 1100°C	62
	5.1.1.2.1.2. Results for equilibration at 1000°C	63
	5.1.1.2.1.3. Results for equilibration at 900°C	64
	5.1.1.2.1.4. Results for equilibration at 700°C	65
	5.1.1.2.2. Micro-PIXE	68
	5.1.1.2.2.1. Results for equilibration at 1100°C	68
	5.1.1.2.2.2. Results for equilibration at 1000°C	68
	5.1.1.2.2.3. Results for equilibration at 900°C	71
5.2.	The Cu-S system	72



5.2.1. CU-RICH MELT - S-RICH MELT ASSEMBLAGE (1200°C)
5.2.1.1. EPMA results	
5.2.1.2. PIXE results	73
5.2.1.2.1. Milli-PIXE	73
5.2.1.2.1.1. Results for equilibration at 1200°C	73
5.2.2. COPPER - DIGENITE ASSEMBLAGE (1000°C AND 800°C	C) 76
5.2.2.1. EPMA results	
5.2.2.2. PIXE results	
5.2.2.2.1. Milli-PIXE	
5.2.2.2.1.1. Results for equilibration at 1000°C	
5.2.2.2.1.2. Results for equilibration at 800°C	79
5.2.2.2.2. Micro-PIXE	80
5.2.2.2.1. Results for equilibration at 1000°C	80
5.2.3. DIGENITE – CU-S MELT ASSEMBLAGE (1000°C)	81
5.2.3.1. EPMA results	81
5.2.3.1.1. Separated drop	82
5.2.3.2. PIXE results	84
5.2.3.2.1. Micro-PIXE	84
5.2.3.2.1.1. Results for equilibration at 1000°C	84
5.3. The Fe-S (±O) system	85
5.3.1. IRON – FE-S MELT ASSEMBLAGE (1200°C TO 1000°C) .	86
5.3.1.1. EPMA results	86
5.3.1.2. PIXE results	92
5.3.1.2.1. Milli-PIXE	
5.3.1.2.1.1. Results for equilibration at 1200°C	
5.3.1.2.1.2. Results for equilibration at 1100°C	93
5.3.1.2.1.3. Results for equilibration at 1000°C	
5.3.2. PYRRHOTITE – FE-S MELT ASSEMBLAGE (1100°C)	97
5.3.2.1. EPMA results	97
5.3.2.2. PIXE results	
5.3.2.2.1. Milli-PIXE	



5.3.3. IRON - TROILITE ASSEMBLAGE (900°C)	99
5.3.3.1. EPMA results	99
5.3.3.2. PIXE results	99
5.3.3.2.1. Milli-PIXE	99
5.3.3.2.1.1. Results for equilibration at 900°C	99
6. DISCUSSION	.102
6.1. The Ni-S system	102
6.1.1. NICKEL - NI-S MELT ASSEMBLAGE (1100°C - 700°C)	102
6.1.1.1. Variation of partition coefficients with different instruments	104
6.1.1.2. Variation of partition coefficient with equilibration temperature	106
6.1.1.3. Variation of partition coefficient with PGE content	109
6.1.1.4. Variation of partition coefficient with resulting from the effect of	
PGE on each other	111
6.1.1.5. In conclusion	111
6.2. The Cu-S system	111
6.2.1. CU-RICH MELT - S-RICH MELT ASSEMBLAGE (1200°C)	111
6.2.1.1. Variation of partition coefficient with PGE content	112
6.2.1.2. Variation of partition coefficient with resulting from the effect of	
PGE on each other	112
6.2.1.3. In conclusion	113
6.2.2. COPPER - DIGENITE ASSEMBLAGE (1000°C AND 800°C)	113
6.2.2.1. Variation of partition coefficient with different instruments	114
6.2.2.2. Variation of partition coefficient with equilibration temperature	114
6.2.2.3. Variation of partition coefficient with PGE content	115
6.2.2.4. Variation of partition coefficient with resulting from the effect of	
PGE on each other	115
6.2.2.5. In conclusion	116
6.2.3. DIGENITE - MELT ASSEMBLAGE (1000°C)	116
6.2.3.1. Variation of partition coefficient with resulting from the effect of	



PGE on each other 117
6.2.3.2. Variation of partition coefficient with PGE content
6.2.3.3. In conclusion 117
.3. The Fe-S system
6.3.1. IRON - FE-S MELT ASSEMBLAGE (1200°C TO 1000°C) 118
6.3.2. PYRRHOTITE – SULPHIDE MELT ASSEMBLAGE (1100°C) 119
6.3.3. IRON - TROILITE ASSEMBLAGE (900°C)120
.4. Mass balance calculations

1. The Ni-S system	125
2.2. The Cu-S system	126
7.3. The Fe-S(±O) system.	127
4. PGE partitioning in general	128

ACKNOWLEDGEMENTS	
REFERENCES	
APPENDIX: TABLES OF EXPERIMENTAL COMPOSIT	IONS AND
CONDITIONS	



LIST OF TABLES

Table 1	Assemblage of the Ni-S system that was investigated,	25
Table 2	Assemblages of the Cu-S system that were investigated	28
Table 3	Assemblages of the Fe-S system that were investigated	36
Table 4	Detection limits obtained for the PGE by milli-PIXE	45
Table 5	Repeated measurement of the S-rich melt of experiment HU443, showing a relationship between total counts collected and detection	
	limit	46
Table 6	Evaluation of filter thickness and acceleration voltage	52
Table 7	Detection limits obtained for the PGE by micro-PIXE	54
Table 8	Major element compositions, determined by EPMA, of co-existing nickel and quenched melt equilibrated at 1100°C	58
Table 9	Major element compositions, determined by EPMA, of co-existing	20
	nickel and quenched melt equilibrated at 1000°C	59
Table 10	Major element compositions, determined by EPMA, of co-existing nickel and quenched melt equilibrated at 900°C	60
Table 11	Major element compositions, determined by EPMA, of co-existing	
	nickel and quenched melt, equilibrated at 700°C	61
Table 12	Milli-PIXE trace element spot analyses of nickel that co-exists with	
	melt, equilibrated at 1100°C	62
Table 13	Milli-PIXE trace element spot analyses of the melt phase that co-exists	
	with nickel, equilibrated at 1100°C.	62
Table 14	Milli-PIXE trace element analyses of nickel that co-exists with melt,	
	equilibrated at 1000°C	63
Table 15	Milli-PIXE trace element analyses of the melt phases that co-exist with	
	nickel, equilibrated at 1000°C	64
Table 16	Milli-PIXE trace element analyses of nickel that co-exists with melt,	
	equilibrated at 900°C	65
Table 17	Milli-PIXE trace element analyses of the melt phases that co-exist with	
	nickel equilibrated at 900°C.	65



Table 18	Milli-PIXE trace element analyses of nickel that co-exists with mel
Tuble 10	equilibrated at 700°C
Table 19	Milli-PIXE trace element analyses of the melt phases of experiment
	equilibrated at 700°C
Table 20	Milli-PIXE analyses of nickel and Ni-S melt in experiments of the Ni-S
	system
Table 21	Micro-PIXE trace element analyses of nickel that co-exists with mel
2722	equilibrated at 1100°C.
Table 22	Micro-PIXE trace element analyses of the melt phases that co-exist with
	nickel, equilibrated at 1100°C
Table 23	Micro-PIXE trace element analyses of nickel that co-exists with melt
	equilibrated at 1000°C
Table 24	Micro-PIXE trace element analyses of the melt phases that co-exist with
	nickel equilibrated at 1000°C.
Table 25	Micro-PIXE trace element analyses of nickel that co-exists with melt
	equilibrated at 900°C
Table 26	Micro-PIXE trace element analyses of the melt phases that co-exist with
	nickel equilibrated at 900°C.
Table 27	Results of micro-PIXE analyses of nickel and Ni-S-melt in experiment
	of the Ni-S system.
Table 28	Major element compositions, determined by EPMA, of co-existing Cu
	rich melt and S-rich melt equilibrated at 1200°C
Table 29	Milli-PIXE trace element analyses of the Cu-rich melt phase co-existing
	with the S-rich melt phase equilibrated at 1200°C
Table 30	Milli-PIXE trace element analyses of the S-rich melt phases co-existing
	with Cu-rich melt phases, equilibrated at 1200°C.
Table 31	Results of milli-PIXE analyses of Cu-rich melt and S-rich melt in
	experiments of the Cu-S system
Table 32	Major element compositions, determined by EPMA, of co-existing
	copper and digenite equilibrated at 1000°C



Table 33	Major element compositions, determined by EPMA, of co-existing	
	copper and digenite equilibrated at 800°C	77
Table 34	Milli-PIXE trace element analyses of copper that co-exists with	
	digenite, equilibrated at 1000°C.	78
Table 35	Milli-PIXE trace element analyses of digenite that co-exists with	
	copper, equilibrated at 1000°C.	78
Table 36	Milli-PIXE trace element analysis of copper that co-exists with digenite,	
	equilibrated at 800°C	79
Table 37	Milli-PIXE trace element analyses of the digenite that co-exists with	
	copper, equilibrated at 800°C	79
Table 38	Results of milli-PIXE analyses of the copper - digenite assemblage in	
	experiments of the Cu-S system	79
Table 39	Micro-PIXE trace element analysis of copper that co-exists with	
	digenite, equilibrated at 1000°C	80
Table 40	Micro-PIXE trace element analyses of digenite that co-exists with	
	copper, equilibrated at 1000°C.	80
Table 41	Results of micro-PIXE analyses of the copper - digenite assemblage in	
	experiments of the Cu-S system	80
Table 42	Major element compositions, determined by EPMA, of co-existing melt	
	and digenite equilibrated at 1000°C	81
Table 43	Micro-PIXE trace element analyses of digenite co-existing with melt,	
	equilibrated at 1000°C	84
Table 44	Micro-PIXE trace element analyses of melt co-existing with digenite,	
	equilibrated at 1000°C	84
Table 45	Results of micro-PIXE analyses of the digenite - melt assemblage in	
	experiments of the Cu-S system	85
Table 46	Major element compositions, determined by EPMA, of co-existing iron	
	and quenched melt (containing O) equilibrated at 1200°C	86
Table 47	Major element compositions, determined by EPMA, of co-existing iron	
	and quenched melt (possibly coexisting with oxides), equilibrated at	
	1100°C	87



Table 48	Major element compositions, determined by EPMA, of co-existing iron	
	and quenched melt equilibrated at 1000°C. Some of the metal contains	
	oxides, and some of the sulphide melts oxygen, which influenced the	
	analyses	92
Table 49	Milli-PIXE trace element analyses of the metal that co-exists with melt	
	in the Fe – S \pm O system, equilibrated at 1200°C	93
Table 50	Milli-PIXE trace element analyses of the melt that co-exists with metal	
	in the Fe – S \pm O system, equilibrated at 1200°C	93
Table 51	Milli-PIXE trace element analyses of the metal that co-exists with melt	
	in the Fe – S \pm O system, equilibrated at 1100°C	94
Table 52	Milli-PIXE trace element analyses of the melt that co-exists with metal	
	in the Fe - S \pm O system, equilibrated at 1100°C	94
Table 53	Milli-PIXE trace element analyses of the metal that co-exists with melt	
	in the Fe-S (±O) system, equilibrated at 1000°C	95
Table 54	Milli-PIXE trace element analyses of the melt that co-exists with metal	
	in the Fe-S (±O) system, equilibrated at 1000°C	96
Table 55	Results of milli-PIXE analyses of the iron - sulphide melt assemblage in	
	experiments of the Fe - S system	96
Table 56	Major element compositions, determined by EPMA, of co-existing	
	pyrrhotite and quenched melt equilibrated at 1100°C	97
Table 57	Milli-PIXE trace element analyses of the melt that co-exists with	
	pyrrhotite in the Fe-S system, equilibrated at 1100°C	98
Table 58	Milli-PIXE trace element analyses of the pyrrhotite that co-exists with	
	melt in the Fe-S system, equilibrated at 1100°C	98
Table 59	Results of milli-PIXE analyses of the melt-pyrrhotite assemblage in	
	experiments of the Fe-S system	98
Table 60	Major element compositions, determined by EPMA, of co-existing iron	
	and troilite equilibrated at 900°C	99
Table 61	Milli-PIXE trace element analyses of iron that co-exists with troilite in	
art from	the Fe-S system, equilibrated at 900°C.	100



Table 62	Milli-PIXE trace element analyses of the troilite that co-exists with	
	metal in the Fe-S system, equilibrated at 900°C	100
Table 63	Results of milli-PIXE analyses of the iron-troilite assemblage in	
	experiments of the Fe-S system	101
Table 64	D (metal/melt) for the PGE determined for Ni metal and melt	
	assemblages from the milli-PIXE results in Table 20	103
Table 65	D (metal/melt) for the PGE determined for Ni metal and melt	
	assemblages from the micro-PIXE results in Table 27	103
Table 66	PGE contents in nickel and sulphide melt determined by both milli- and	
	micro-PIXE	105
Table 67	D(Cu-rich melt/S-rich melt) for the PGE determined for the Cu-rich	
	melt and S-rich melt from milli-PIXE results in Table 31	112
Table 68	D(copper/digenite) for the PGE determined for copper and digenite	
	from milli-PIXE results in Table 38.	114
Table 69	D(copper/digenite) for the PGE determined for copper and digenite	
	from micro-PIXE results in Table 41	114
Table 70	D(melt/digenite) for the PGE determined for the melt and digenite from	
	micro-PIXE results in Table 45	117
Table 71	D(iron/melt) for the PGE determined from milli-PIXE results in Table	
	55	119
Table 72	D(melt/pyrrhotite) for the PGE determined from milli-PIXE results in	
	Table 59	120
Table 73	D(iron/troilite) for the PGE determined from milli-PIXE results in	
	Table 63	120
Table 74	Mass balance errors calculated from micro-PIXE analyses of PGE	
	contents of the Ni-S system, expressed as percentages of the original	
	PGE content.	121
Table 75	Mass balance errors calculated from milli-PIXE analyses of PGE	
	contents of the Ni-S system, expressed as percentages of the original	
	PGE content	122



LIST OF FIGURES

Figure 1	The sealed quartz glass tube technique	14	
Figure 2	Sealing of experimental tube under vacuum		
Figure 3	The reduction of Cu and Ni at 600°C		
Figure 4	Reduction of Fe after being weighed into an experimental		
	tube	15	
Figure 5	Chamber furnace fitted with six tubes	17	
Figure 6	Experiment HU393, co-existing nickel and quenched melt, equilibrated at 1000°C		
Figure 7	Experiment HU465, co-existing copper (with digenite inclusions)		
	and digenite, equilibrated at 1000°C.	22	
Figure 8	Experiment HU420, co-existing digenite (twinned) and quenched		
	melt, equilibrated at 1000°C.	22	
Figure 9	Experiment HU442, co-existing immiscible Cu-rich melt and S-rich		
	melt, equilibrated at 1200°C.	23	
Figure 10	Experiment HU436, co-existing iron and troilite, equilibrated at		
	900°C	23	
Figure 11	Experiment HU736, Fe-S melt that co-exists with iron (not visible in		
	this photograph), equilibrated at 1100°C.	24	
Figure 12	Phase diagram of the Ni-S system, after Sharma and Chang (1980)		
	and Cemic and Kleppa (1986).	26	
Figure 13	Experiment HU412, co-existing nickel and quenched melt,		
	equilibrated at 1000°C.	27	
Figure 14	Experiment HU426, co-existing nickel and quenched melt, equilibrated at 900°C.	27	
Figure 15	Phase diagram of the Cu-S system after Chakrabarti and Laughlin		
	(1986)	29	
Figure 16	Phase diagram of the Cu-S system after Chakrabarti and Laughlin		
	(1986). showing co-existing digenite and sulphide melt	30	



Figure 17	Experiment HU421, co-existing copper and digenite, equilibrated at
	900°C. Sulphide blebs scattered through the metal vary in size from
	extremely small to large.
Figure 18	Experiment HU423, co-existing copper (with small inclusions of Cu
	sulphide) and digenite, equilibrated at 900°C.
Figure 19	Experiment HU467, co-existing Cu melt and digenite, equilibrated
	at 1100°C. The Cu melt contains small sulphide blebs
Figure 20	Experiment HU467, digenite with quenched Cu melt filling the
	cracks, equilibrated at 1100°C
Figure 21	Experiment HU445, co-existing immiscible Cu-rich and S-rich
	melts, equilibrated at 1200°C. The sulphide melt rim broke away
	from this central section during mounting, but sulphide melt is also
	observed as small and larger spheres dispersed through the Cu melt
Figure 22	Experiment HU445, equilibrated at 1200°C. S-rich melts as found
	around the rim of the experiment shown in Photograph 21, with Cu-
	rich melt present as small spheres scattered through the sulphide
	melt
Figure 23	Experiment HU418, co-existing digenite and quenched melt,
	equilibrated at 1000°C. In the absence of well-developed twinning
	in the digenite, the melt phase can only be identified by its
	heterogeneous appearance
Figure 24	Phase diagram of the Fe-S system after Chuang et al. (1985)
Figure 25	Experiment $HU/34$, containing iron and sulphide meit, equilibrated
	at 1100 C. The sulphide ment appears nonogeneous on this scale,
Figure 26	Experiment H11730, containing co existing purchatite and quenched
Figure 20	sulphide melt equilibrated at 1100°. The melt can be distinguished
	from the sulphide only by its slightly beterogeneous appearance
Figure 27	Experiment HU436, containing troilite and dendritic iron
Burnet	equilibrated at 900°C



Figure 28	The influence of counts collected on the detection limit of Pt in the	
	S-rich melt of experiment HU443	46
Figure 29	Experiment HU429, co-existing nickel and quenched melt,	
	equilibrated at 900°C. The red rectangles indicate the size and	
	shapes of the areas analysed by micro-PIXE by moving the beam	
	across the sample, and the blue ovals indicate the size and shape of	
	the milli-PIXE spots, which are elongated to ovals due to the 45°	
	angle of incidence with the incoming beam.	48
Figure 30	Milli-PIXE spectrum acquired at 2.45 MeV on quenched Ni-S melt	
	of experiment HU429, no filter.	49
Figure 31	Spectrum fitted with GUPIX (yellow) to determine composition.	
	Fitted for Ni, Rh and Pd	50
Figure 32	Milli-PIXE spectrum acquired at 2.45 MeV on quenched Ni-S melt	
	of experiment HU429, 125 µm Al filter	51
Figure 33	Milli-PIXE spectrum acquired at 3.00 MeV on quenched Ni-S melt	
	of experiment HU429, 125 µm Al filter	52
Figure 34	Damage caused by the milli-PIXE beam in the carbon coating on the	
	surface of Fe-S melt	53
Figure 35	Separated drop from experiment HU392 with nickel and quenched	
	melt equilibrated at 1000°C	60
Figure 36	Co-existing nickel and quenched melt of experiment HU733 that	
	was equilibrated at 1100°C. The experiment contained a bulk of 500	
	ppm each of Rh, Pd and Pt	63
Figure 37	Experiment HU472 consisting of nickel and melt that was	
	equilibrated at 700°C. The small area of nickel was not found during	
	milli-PIXE analysis	67
Figure 38	The separated drop from experiment HU397. Bright subhedral	
	crystals (Cu, S, Rh, Pt) and a highly heterogeneous matrix can be	
	distinguished	83
Figure 39	Experiment HU397 that consists of co-existing digenite and melt.	
	The experiment was equilibrated at 1000°C	83



Figure 40	Experiment HU825 contains heterogeneously quenched melt and	
	iron. The appearance of the quenched melt is very unusual	88
Figure 41	Enlargement of the dendrites of experiment HU825, shown in	
	Figure 40. The dull grey dendrites were determined by electron	
	microscopy to have high contents of Fe-oxide along with Fe	88
Figure 42	Experiment HU845 contains metal and melt that were equilibrated at	
	1000°C. Both phases contain Fe oxides (grey inclusions)	90
Figure 43	Enlargement of the metal and melt phases of experiment HU845	
	shown in Figure 42. The grey oxides are scattered through the metal.	90
Figure 44	Experiment HU844 was supposed to contain metal and melt that	
	were equilibrated at 1000°C. The "metal" phase is unrecognisable	
	due to the low reflectivity oxides scattered all through it	91
Figure 45	Higher magnification of the "metal" phase of experiment HU844	
	shown in Figure 44. Large Fe-oxide crystals are visible, implying	
	oxidation at a late stage	91
Figure 46	Comparison of PGE contents determined by milli-PIXE and micro-	
	PIXE in corresponding phases from experiments HU393, HU427	
	and HU429	105
Figure 47	D of experiments HU733 and HU469 plotted against temperature.	
	Both experiments contained 500 ppm of each PGE	106
Figure 48	D of experiments HU381 and HU429 plotted against temperature	107
Figure 49	D of experiments HU393 and HU753 plotted against temperature.	
	Both experiments contained 1000 ppm of each PGE	107
Figure 50	D of experiments HU731 and HU471 plotted against temperature	108
Figure 51	D of experiments HU441 and HU429 plotted against temperature.	
	Both experiments contained 2000 ppm of each PGE	108
Figure 52	D of experiments HU393 and HU381 plotted against PGE content.	
	Both experiments were equilibrated at 1000°C	109
Figure 53	D of experiments HU753 and HU429 plotted against PGE content.	
	Both experiments were equilibrated at 900°C	110



Figure 54	D of experiments HU393, HU394, HU395 and HU412 plotted	
	1000°C	110
Figure 55	D of experiments HU442 and HU450 plotted against PGE content.	
	Both experiments were equilibrated at 1200°C	113
Figure 56	D_{Rh},D_{Pd} and D_{Pt} of experiments HU387 and HU482 plotted against	
	equilibration temperature. Both experiments contained 1000 ppm of	
	each PGE	115
Figure 57	D of experiments HU385, HU387 and HU465, plotted against PGE	
	content. All were equilibrated at 1000°C	116
Figure 58	D of experiments HU398, HU411 and HU413 plotted against PGE	
	content. All were reacted at 1000°C	118
Figure 59	The linear relationship between mass calibration errors and standard	
	deviation errors for micro-PIXE data at 1100°C, 1000°C and 900°C	
	indicated by the regression lines	123
Figure 60	The linear relationship between mass calibration errors and standard	
	deviation errors for milli-PIXE data at 1100°C, 1000°C, 900°C and	
	700°C indicated by the regression lines	123





LIST OF ABBREVIATIONS AND SYMBOLS

σ	standard deviation	
AEC	Atomic Energy Corporation	
at%	Atomic percent	
bd	below detection	
D	Nernst partition coefficient	
Dx	Nernst partition coefficient for element X	
ED	energy dispersive	
Exp	experiment number	
eV	electron volt	
EPMA	electron probe micro analyser	
FWHM	full width at half maximum	
KeV	kilo electron volt	
LLD	lower limit of detection	
MeV	mega electron volt	
mss	monosulphide solid solution	
nA	nano Ampére	
n	number of analyses per experiment	
nd	not determined	
NAC	National Accelerator Center	
nC	nano Coulomb	
pA	pico Ampére	
PGE	platinum-group element(s)	
PIXE	particle induced X-ray emission	
PRF	pre-reaction furnace	
ppm	parts per million	
SEM	scanning electron microscope	
Temp	temperature	
WD	wavelength dispersive	
wt%	weight percent	

xviii



LIST OF MINERAL FORMULAE - ALL PHASES SYNTHETIC

Cu	Copper
CuS	Covellite
Cu _{2-x} S	Digenite
Cu ₂ S	Chalcocite
CuFeS ₂	Chalcopyrite
Fe	Iron
FeS	Troilite
FeS _{1+x}	Pyrrhotite
FeS ₂	Pyrite
(Fe,Ni) ₉ S ₈	Pentlandite
Ni	Nickel
NiS	Millerite
NiS ₂	Vaesite
Ni_3S_2	Heazlewoodite
Ni ₉ S ₈	Godlevskite
Ni ₃ S ₄	Polydymite