

1445740

THESIS

LG

712

-M99

no 87

copy 1

MECHANISMS OF PLATINUM-GROUP ELEMENT FRACTIONATION IN ULTRAMAFIC MELTS AND IMPLICATIONS FOR THE EXPLORATION FOR MAGMATIC NICKEL SULPHIDE DEPOSITS

Marek Locmelis

GEMOC ARC National Key Centre, Department of Earth and Planetary Sciences,
Macquarie University

Sydney, Australia

This thesis is presented for fulfilment of the degree of Doctor of Philosophy. May 2010

TABLE OF CONTENTS

Table of contents.....	3
List of figures	11
List of tables.....	17
Abstract.....	21
Declaration.....	23
Acknowledgements	25
Chapter 1 - Introduction	27
1.1 Introduction.....	27
1.2 Aims and objectives.....	30
1.3 Organization and Overview of the Thesis	31
1.4 Industry collaborations	33
Chapter 2 - Komatiites, komatiitic basalts and ferro-picrites: petrogenesis and geochemistry	35
2.1 Komatiites, komatiitic basalts and ferro-picrites.....	35
2.2 Komatiite Mineralogy.....	36
2.3 Komatiite Geochemistry.....	38
2.3.1 Behaviour of PGE during fractionation	40
2.3.2 PGE contents in komatiites.....	41
2.4 Komatiite-hosted nickel-sulphide deposits	41
2.4.1 Sulphide saturation in komatiites.....	44
2.4.2 Onset of sulphide saturation in Type-1 and Type-2 deposits	45
2.5 PGE mineralisation in komatiites	45

Chapter 3 - Localities & sample settings 49

3.1 Introduction..... 49

3.2 Sampling strategy and key variables..... 49

3.2.1 Cratons and greenstone belts49

3.2.2 Age 50

3.2.3 Magma types and petrogenetic affinity..... 50

3.2.3 Mineralisation style and endowment 50

3.2.5 Emplacement characteristics..... 51

3.2.6 Metamorphic grade and nature of secondary alteration..... 51

3.3 Samples and Localities 54

3.3.1 Samples 54

3.3.2 Eastern Goldfields Superterrane in the Yilgarn Craton..... 54

3.3.3 Superior Craton 65

3.3.4 Fennoscandian Craton 66

Chapter 4 – Analytical Methods 71

4.1 Introduction..... 71

4.2 Whole-rock analytical techniques..... 71

4.2.1 Major, minor and trace elements..... 71

4.3 In-situ analytical techniques 72

4.3.1 Sample preparation 72

4.3.2 Electron-microprobe analysis 72

4.3.3 Laser Ablation ICP-MS..... 73

4.4 Platinum-group element whole-rock data 74

4.5 Carius tube digestion isotope dilution ICP-MS..... 76

4.5.1 Isotope Dilution ICP-MS 77

4.5.2 Carius Tube Digestion & PGE Extraction 79

4.5.3 ICP-MS solution analysis for PGE 81

4.5.4 Accuracy and precision of the PGE analysis 82

Chapter 5 - Petrography & Mineral chemistry.....	83
5.1 Introduction.....	83
5.2 Chromite	83
5.2.1 Petrography	83
5.2.2 Chromite chemistry.....	84
5.3 Olivine.....	97
5.3.1 Introduction.....	97
5.3.2 Samples and Petrography.....	97
5.3.3 Results	98
5.3.4 Discussion.....	100
5.3.5 Conclusions	106
5.4 Sulphides.....	113
5.4.1 Introduction.....	113
5.4.2 Samples.....	113
5.4.3 Results.....	113
Chapter 6 – Whole-rock chemistry	117
6.1 Introduction.....	117
6.2 Results.....	117
6.2.1 Major and minor element chemistry.....	117
6.2.2 Platinum-group element chemistry.....	118
6.3 Discussion.....	121
6.3.1 Major and minor element chemistry.....	121
Chapter 7 - In-situ laser ablation ICP-MS analysis of ruthenium in chromite	133
7.1 Introduction.....	133
7.2 Samples	133
7.3 Analytical methods	135
7.3.1 In-situ laser ablation ICP-MS analysis	135

7.4 Results	140
7.4.1 In-situ laser Ablation ICP-MS	140
7.4.2 Carius tube digestion isotope dilution ICP-MS	147
7.5 Discussion	148
7.6 Conclusions	149
 Chapter 8 – Ruthenium in chromite from komatiites, komatiitic basalts, and ferro-picrites	 155
8.1 Introduction	155
8.2 Results	155
8.2.1 Interpretation of the Ru compilation plots	155
8.2.2 Ruthenium variability in chromite	156
8.3 Discussion	164
8.3.1 Ruthenium variation in chromite	164
8.3.2 Ru contents vs chromite composition	166
8.3.3 The role of oxygen fugacity	170
8.3.4 Other factors controlling the fractionation and concentration of Ru	172
8.3.5 Timing of sulphide saturation	173
8.3.6 The significance of single high-Ru grains	176
8.4 Conclusions	176
 Chapter 9 - Anomalous sulphur-poor platinum-group element mineralisation in komatiitic cumulates, Mount Clifford, Western Australia	 179
9.1 Introduction	179
9.1.1 Models for the origin of PGE mineralisation	179
9.2 Sampling and Analytical Methods	181
9.3 Results	181
9.3.1 Petrography and Mineralogy	181
9.3.2 Platinum-group Minerals	183
9.3.3 Whole-rock Geochemistry	187

9.4 Discussion.....	193
9.5 Conclusions.....	197
 Chapter 10 - The role of chromite, olivine and platinum-group minerals in the fractionation and concentration of platinum-group elements	 199
10.1 Introduction.....	199
10.2 Samples and methodology.....	199
10.3 Results	200
10.3.1 Chromite	200
10.3.2 Olivine.....	200
10.3.3 Platinum-group minerals.....	203
10.4 Discussion.....	204
10.4.1 PGE contents of the chromite separates.....	205
10.4.2 PGE contents of the olivine separates.....	209
10.4.3 Formation of platinum-group minerals.....	211
10.5 Conclusions.....	212
 Chapter 11 – Ruthenium content of chromite: Implications for the exploration for magmatic nickel-sulphide deposits	 213
11.1 Introduction	214
11.2 Chromite and olivine trace element composition as indicator for nickel-sulphide mineralisation	214
11.2.1 Chromite.....	214
11.2.2 Olivine.....	215
11.3 Limitations of the whole-rock approach and advantages of the in-situ LA-ICP-MS studies	216
11.4 False positives	216
11.5 Ideas for future research.....	217
11.5.1 Vectors towards massive ore zones	218

11.6 Conclusions	219
-------------------------------	------------

Chapter 12 - Conclusions: The petrogenesis of komatiites and komatiite-derived melts – new insights from high accuracy and precision platinum-group element analysis.....	223
--	------------

References	225
-------------------------	------------

Appendix	243
-----------------------	------------

Appendix 1: Major and trace element composition of chromite and olivine	245
---	-----

Appendix 2: Laser Ablation ICP-MS analysis of Ru in chromite	345
--	-----

Appendix 3: Whole-rock analyses	369
---------------------------------------	-----

Appendix 4: Publication	379
-------------------------------	-----

List of Figures

Figure 2-1: Idealised cross-section through a fully differentiated, layered komatiite flow.....	36
Figure 2-2: Phase relations for komatiites after Arndt, (1976).....	38
Figure 2-3: Pt/Ti vs age of komatiites from selected localities and petrogenetic affinity	42
Figure 3-1: Komatiite world location map.....	53
Figure 3-2: Locality map of the Eastern Goldfields Superterrane of the Yilgarn Craton illustrating its high nickel-sulphide endowment.	56
Figure 3-3: Stratigraphy of the Mount Clifford dunite body	58
Figure 3-4: Idealised stratigraphy of the Betheno dunite body showing the position of the samples MKT 528 – 107.3, 173.25, 277.9, and 429.4.....	59
Figure 3-5: Stratigraphy of drill core CCD11a in the Cliffs Ultramafic Belt	59
Figure 3-6: Intersection through the overturned sequence at The Horn, borehole LWDD-754.....	60
Figure 3-7: Stratigraphy of the Airport Ultramafic / Wiluna	61
Figure 3-8: Microscope image of the dendritic olivine texture at Murphy Well, transmitted light.	62
Figure 3-9: Simplified stratigraphy of borehole BSD-64	63
Figure 3-10: Stratigraphy of Collurabbie's Beta Horizon.....	64
Figure 3-11: Location map of the Abitibi Greenstone belt, showing Fred's Flow (FF) and the Boston Creek Flow (BCF).....	66
Figure 3-12: Locality map of the Central Lapland Greenstone Belt (CLGB)	67
Figure 3-13: Locality map of Pechenga.....	68
Fig 4-1: Propagated error for ID resulting from varying isotopic ratios in the sample and spike (x/y).....	79
Figure 5-1: Back-scattered electron images of chromites.....	85
Figure 5-2: Compositions of chromites from komatiites in (A) a trivalent cation plot Fe vs. Cr vs. Al; and (B) magnified for the relevant proportion.	87
Figure 5-3: TiO_2 vs. $\text{Fe}^{3+}/(\text{Cr}+\text{Al}+\text{Fe}^{3+})$ and ZnO, NiO, and MnO vs. $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ in chromites from komatiites.	88
Figure 5-4: Compositions of chromites from komatiitic basalts and ferropicrites in the trivalent cation plot Fe vs. Cr vs. Al	88

List of figures

Figure 5-5: TiO_2 vs. $\text{Fe}^{3+}/(\text{Cr}+\text{Al}+\text{Fe}^{3+})$ and ZnO , NiO , and MnO vs. $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ in chromites from komatiitic basalts and ferro-picrites.	89
Table 5-1: Representative electron micro-probe analysis of chromites from komatiites.	90
Table 5-1 (continued): Representative electron micro-probe analysis of chromites from komatiites.	91
Table 5-1 (continued): Representative electron micro-probe analysis of chromites from komatiites.	92
Table 5-1 (continued): Representative electron micro-probe analysis of chromites from komatiites.	93
Figure 5-6: Transmitted light microscope images of the sample mineralogy.....	99
Figure 5-7: Nickel content of olivine vs the forsterite (Fo) content	102
Figure 5-8: Chromium content of olivine vs the forsterite content	103
Figure 5-9: Calcium content of olivine vs the forsterite content	104
Figure 5-10: Trace element concentrations of olivine vs. MgO	107
Figure 5-10 (continued): Trace element concentrations of olivine vs. MgO	108
Figure 5-10 (continued): Trace element concentrations of olivine vs. MgO	109
Figure 5-11: Backscattered electron images of the sample mineralogy	114
Figure 5-11: C1 chondrite normalised PGE plots for sulphides from Betheno.....	114
Figure 6-1: Al_2O_3 vs. TiO_2 in komatiites and komatiitic basalts	119
Figure 6-2: Al_2O_3 , SiO_2 , FeO . and Ni vs. MgO in komatiites and komatiitic basalts.....	119
Figure 6-3: Sulphur vs. Ni in komatiites and komatiitic basalts.....	120
Figure 6-4: Whole-rock Pt and Pd contents vs. MgO and Cr of rocks investigated within this study.	120
Figure 6-4 (continued): Whole-rock Ru and Ir contents vs. MgO and Cr of rocks investigated within this study.....	121
Figure 6-5: Theoretical Cr – MgO compositions of komatiitic liquids and cumulates after Barnes (1998).	122
Figure 6-6: Chromium– MgO compositions of the samples investigated in this study.	123
Figure 6-7: C1-chondrite normalised PGE and Ni plots of komatiites.....	125
Figure 6-7 (continued): C1-chondrite normalised PGE and Ni plots of komatiites.....	126

Figure 6-8: C1 chondrite normalised PGE and Ni plots of komatiitic basalts and ferro-picrites.	126
Figure 6-9: C1 chondrite normalised [N] Pd/Ir and Pd/Ru vs MgO of the samples included in this study of komatiitic basalts and ferro-picrites.	127
Figure: 6-10: Whole-rock Ru-Cr variation in S-poor (<0.25 wt %) komatiites from the Agnew Wiluna Belt.	129
Figure 7-1: BSE images of chromite in komatiite and komatiitic basalt.....	134
Figure 7-2: Comparison of nickel values obtained from electron microprobe analysis and laser ablation ICP-MS analysis	136
Figure 7-3: Ruthenium concentrations as analyzed by LA-ICP-MS	141
Figure 7-4: Repeated Ru analysis of the PGE-A	142
Figure 7-5: Repeated Ru analysis of the LCR-1 chromite.....	142
Figure 7-6: Ruthenium in komatiitic chromite as analyzed by LA-ICP-MS.....	145
Figure 7-7: Time resolved analysis diagram obtained by LA-ICP-MS illustrating....	146
Figure 8-1: Ruthenium concentrations in chromite grains from komatiites.	157
Figure 8-2: Ruthenium in chromites from komatiitic basalts.....	158
Figure 8-3: Ruthenium in chromites from ferro-picrites	159
Figure 8-4: Major and trace element composition of chromites from komatiites (left) and komatiitic basalts (right)	168
Figure 8-4 (continued): Major and trace element composition of chromites from komatiites (left) and komatiitic basalts (right).....	169
Figure 8-4: Major and trace element composition of chromites from komatiites (left) and komatiitic basalts (right).	170
Figure 8-5: Plot of Ru vs. $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ for (A) chromite from komatiites and (B) komatiitic basalts and ferro-picrites.....	172
Figure 9-1: Sulphide inclusion in chromite grains.....	182
Figure 9-2: Backscatter electron images of the sample mineralogy	185
Figure 9-3: Mineral chemistry of Pd-antimonides.....	186
Figure 9-4: Geochemical profile down drill hole LMCD-009.	188
Figure 9-5: Detailed geochemical profile through the PGE-rich zone.	189

List of figures

Figure 9-6: (A) Plot of whole-rock Ir vs Pt for Mount Clifford reef samples and from Wiluna Type-3 mineralisation; (B) Plot of whole-rock Ir vs Mg# for Mount Clifford reef samples compared with S-poor komatiitic cumulates (MgO>40%) from global database (predominantly samples from Yilgarn and Abitibi terranes).... 192

Figure 9-7: Ni-Mg# and Co-Mg# whole-rock data..... 193

Figure 10-1: C1 chondrite normalised PGE plots for samples from Kurrajong 201

Figure 10-2: C1 chondrite normalised PGE plots for samples from Betheno 202

Figure 10-3: C1 chondrite normalised PGE plots for samples from Mount Clifford 202

Figure 10-4: C1 chondrite normalised PGE plots for samples from Perseverance 203

Figure 10-5: C1 chondrite normalised PGE plots for a sample from The Horn..... 203

Figure 10-6: X-ray composition maps of sample LWDD-754-319.3 from The Horn. 204

Figure 10-7: SEM image of the sample 9347a from Betheno 204

Figure 10-8: Sulphide inclusion in olivine in a sample from Perseverance 211

Figure 11-1: Whole-rock Ru-Cr variation in S-poor (< 0.6 wt% S) komatiites from the Yilgarn craton. 217

Figure 11-2: Ruthenium concentrations in chromites from The Horn in relationship to the proximity to massive nickel-sulphide mineralisation. 220

Figure 11-3: Geochemical profile down drill core LWDD-754 (The Horn)..... 221

List of Tables

Table 2-1: Main geochemical characteristics of different types of komatiites	40
Table 2-2: Classification of komatiite hosted nickel-sulphide deposits.....	43
Table 3-1: Localities and key variables.	52
Table 3-2: Mineralisation Scores (MinScores) of the localities investigated within this study	54
Table 4-1: Operating parameters of the laser ablation ICP-MS system.....	74
Table 4-2: Results of repeated analyses of BCR-2g by LA-ICP-MS (average value of seven analyses) and comparison with the reference values published by the U.S. Geological Survey (USGS website, May 2010).	74
Table 4-3: Inter-laboratory comparison of PGE analysis between Geolabs and Ultratrace.....	75
Table 4-4: Comparison of duplicate PGE analysis of samples from Perseverance using (a) Carius tube digestion isotope dilution ICP-MS analysis at GEMOC and (b) nickel-sulphide fire-assay analysis at Ultratrace Laboratories.	76
Table 4-5: Operating parameters of the ICP-MS system (PGE solution analysis).....	81
Table 4-6: Repeated analyses of the OKUM reference material.	82
Table 5-2: Representative electron micro-probe analysis of chromites from komatiitic basalts and ferro-picrites.....	94
Table 5-2 (continued): Representative electron micro-probe analysis of chromites .from komatiitic basalts and ferro-picrites.	95
Table 5-2 (continued): Representative electron micro-probe analysis of chromites .from komatiitic basalts and ferro-picrites.	96
Table 5-3: Average major and trace element composition of olivine.	110
Table 5-3 (continued): Average major and trace element composition of olivine.	111
Table 5-3 (continued): Average major and trace element composition of olivine.	112
Table 5-4: Major, trace, and platinum-group element analysis of sulphides. Major elements by EMP, PGE by LA-ICP-MS.	115
Table 5-4 (continued): Major, trace, and platinum-group element analysis of sulphides. Major elements by EMP, PGE by LA-ICP-MS.	116

Table 6-1: Representative whole-rock major, trace, and platinum-group element analyses of samples included in this study. All values are normalised to 100%-volatile free compositions.	130
Table 6-1 (continued): Representative whole-rock major, trace, and platinum-group element analyses of samples included in this study. All values are normalised to 100%-volatile free compositions.	131
Table 6-1 (continued): Representative whole-rock major, trace, and platinum-group element analyses of samples included in this study. All values are normalised to 100%-volatile free compositions.	132
Table 7-1: Operating parameters of the laser ablation ICP-MS system.....	136
Table 7-2: Results of repeated analyses of LCR-1 by LA-ICP-MS and comparison with literature values.	137
Table 7-3: Argide interferences on PGE isotopes in LA-ICP-MS.	140
Table 7-4: Results of repeated analyses of chromite grains from the sample MW (Murphy Well) including 1- σ errors and lower limits of detection (LLD) calculated in Glitter.	147
Table 7-5: Carius tube digestion ID ICP-MS data for Kurrajong chromite concentrations and OKUM standard concentrations obtained during this study. .	148
Appendix Chapter 7-A-A Kurrajong (KJD-A) chromite analysis. Major and trace element analysis by EMP; Ru analysis by LA-ICP-MS.	150
Appendix Chapter 7-A-B Kurrajong (KJD-B) chromite analysis. Major and trace element analysis by EMP; Ru analysis by LA-ICP-MS.	151
Appendix Chapter 7-A-C Murphy Well (MW-2303-8) chromite analysis. Major and trace element analysis by EMP; Ru analysis by LA-ICP-MS.....	152
Appendix Chapter 7-A-D Collurabbie (CLD-46-135.9) chromite analysis. Major and trace element analysis by EMP; Ru analysis by LA-ICP-MS.....	153
Table 8-1: Summary of in-situ laser ablation ICP analyses of Ru in chromites from komatiites.	160
Table 8-1 (continued): Summary of in-situ laser ablation ICP analyses of Ru in chromites from komatiites.	161
Table 8-2: Summary of in-situ laser ablation ICP analyses of Ru in chromites from komatiitic basalts.....	162
Table 8-3: Summary of in-situ laser ablation ICP analyses of Ru in chromites from ferro-picrites.....	163
Table 8-5: Overview of the characteristics of the sampled localities in relation to prospectivity for nickel-sulphide mineralisation.	175
Table 9-1: Representative microprobe analyses of platinum-group minerals.....	184

Table 9-2: Major and trace element concentrations in the PGE-rich zone (Genanalysis data).	191
Table 9-3: Major, trace and PGE concentrations in the PGE-rich zone (GeoScience data).	192
Table 9-4: Representative microprobe analysis of olivine.....	194
Table 10-1: PGE contents of chromite separates. All concentrations in ppb. Values from Puchtel and Humayun (2001) are shown for comparison.	200
Table 10-2: PGE contents of olivine separates. All concentrations in ppb. Representative values from Puchtel and Humayun (2001) are shown for comparison.	201
Table 10-3: Comparison of the Pt/Pd ratios in whole-rock samples and chromite separates from the PGE-reef at Mount Clifford.....	207
Table 10-4: Parameters for the mass balance calculations.....	208
Table 10-5: Results of the mass balance calculations.....	209

ABSTRACT

Platinum-group elements (PGE) are important as petrogenetic tracers, but owing to their low abundances and complex behaviour they are among the least understood elements in geochemistry. This study investigates the mechanisms of PGE fractionation in ultramafic systems (komatiites, komatiitic basalts, ferro-picrites) and focuses on the role of chromite. Samples from a range of occurrences have been analysed to assess potential controls on PGE behaviour, such as geochemical affinities (Munro-type and Karasjok-type), age (2.0 and 2.7 Ga), emplacement styles, metamorphic grade and nickel-sulphide mineralisation endowment and style.

Data obtained by in-situ laser ablation ICP-MS analysis provide the first direct evidence that Ru can exist in solid solution in chromite with concentrations up to several hundred ppb. The data show that the behaviour of Ru is dominantly controlled by the sulphide-saturation state. In systems that did not equilibrate with a sulphide liquid, chromites have distinctly higher Ru concentrations than chromites from systems that interacted with a sulphur-source during crystallisation. Carius tube digestion isotope dilution ICP-MS analyses of chromite separates confirm the accuracy of the in-situ study and also show that Ir is weakly compatible in chromite. Anomalously high Pt and Pd concentrations in chromite separates reflect the presence of platinum-group minerals (PGM) and suggest that PGM are common accessory phases in komatiites. A study of the PGE-mineralogy shows that PGM in komatiites can be of magmatic and post-magmatic origin and that they often remain undetected due to grain sizes less than 5 μm . As a consequence, the presence of PGE minerals has to be taken into account when whole-rock PGE signatures are interpreted.

The association of Ru-poor chromites with Ni mineralisation and Ru-rich chromites with barren systems provides a new tool for the exploration for nickel-sulphide deposits. This model applies to all magma types and is independent of the age, the geochemical affinity, and other sample characteristics.

ACKNOWLEDGEMENTS

This thesis results from the collaboration between Macquarie University / GEMOC and the Centre for Exploration Targeting at the University of Western Australia. This study used instrumentation funded by ARC LIEF and DEST Systematic Infrastructure and Macquarie University. It was supported by an IMURS scholarship and a PGRF travel fund (Higher Degree Research Unit, Macquarie University), by the AMIRA Project P710a, and by the MERIWA grant M388

I want to thank all the people who have been implicated in my work during this PhD project and particularly my official supervisors Norman Pearson, Suzanne O'Reilly, and Marco Fiorentini. I would like to express my special thanks to Steve Barnes who was a great help along the way. I thank my office mates Alan Kobussen, Cara Donnelly, and June Chevet for sharing their knowledge and experience. I also thank all my co-workers at GEMOC who helped me on more than one occasion to solve problems outside my areas of expertise: Kelsie Dadd, Peter Wieland, Mei-Fei Chu, Will Powell, Kevin Grant, Dick Flood, Bill Griffin, Carol McMahon, Sally-Ann Hodgekiss, Michael Engelbretsen, and Nigel Wilson. Also, I thank Belinda Godel, Steve Beresford, and Steve Barnes (yes, again!) for their help during the past years.

Finally, I acknowledge the support and companionship from my friends and family , and particularly my toki Christina.

