Improved in-situ determination of PGE concentration of chromite by LA-ICP-MS: Towards a better understanding

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Abstract. The arrival of new LA-ICP-MS equipment at UQAC allowed us to analyse the Os, Ir, Ru and Rh contents of chromite from samples representative of different geological settings including MORB, boninites, komatiites, continental flood basalt picrite, continental-type and oceanic-type chromitites, and chills of the Bushveld Complex. Our new LA-ICP-MS results combined with previous data confirm that chromite could act as the dominant phase in controlling the whole rock budget of Os, Ir, Ru and Rh, but chromite generally share this role with other phases like PGM whose crystallization seems to be influenced by chromite crystallization. Most primitive mantle normalized PGE profiles of chromite show $Ru_N > Rh_N$ with the exception of boninite and arc lavas which tend to show $Ru_N < Rh_N$. The chromite from each different setting has distinctive PGE normalized profiles that can be used to identify parental magma. For example the chromite from the chills of the Bushveld lies between komatiites and picrite rather than boninite.

Keywords. Laser ablation ICP-MS, chromite, PGE, fractionation, partition coefficients.

1 Introduction

Until recently our understanding of the role of chromite in the fractionation of Os, Ir, Ru, Rh, Pt and Pd (PGE) was essentially indirect and based on the correlations between whole rock Cr and whole rock PGE (Pagé et al. 2012, and references therein). The enrichment of Os, Ir and Ru (IPGE) that is commonly observed in all types of chromitites suggests that chromite somehow concentrates these elements. It was still unclear if the trends observed reflect the presence of platinum-group minerals (PGMs) entrapped in chromite during their crystallization and growth (Finnigan et al. 2008), or the presence of PGE in solid solution within the chromite structure. The main difficulty in answering this question arose because it was not possible to carry accurate measurements of the concentration of the IPGE in chromite by in-situ techniques because of the very low concentrations.

The introduction of in-situ analysis of chromite by laser ablation combined with ICP-MS (LA-ICP-MS) has allowed the measurement of Ru content in chromites from Archean komatiitic lavas (Locmelis et al. 2011; Pagé et al. 2012; Méric et al. 2012) and oxidized arc lavas from the Ambae Volcano in the Vanuatu Island Arc in which Os, Ir, Ru and Rh (≤ 82 ppb, ≤ 200 ppb, ≤ 162 ppb, and ≤ 149 ppb, respectively; Fig. 1a) have been reported (Park et al. 2012).

Chromites from plutonic settings are mostly devoid of measurable concentrations of PGE (Park et al. 2012;

Pagé et al. 2012), apart from the chromite from the Jimberlana layered intrusion where concentrations of Ir ≤ 12 ppb have been reported (Park et al. 2012).

There is now a new generation of LA-ICP-MS which has lower detection limits by an order of magnitude (Savard et al. 2012). We present new results on the concentrations of Os, Ir, Ru, and Rh in chromite from samples from various volcanic and plutonic settings. These new results confirm the role of chromite in the fractionation of PGE in partial melting and fractional crystallization. A better understanding of the role of chromite on the fractionation of PGE has multiple implications; it throws light on the mechanisms and the budgets of the transfer and/or the sequestration of PGE between reservoirs (mantle vs. melt vs. cumulate), on the crystallochemistry of chromite, site occupancies, and partition coefficients. The ambivalent nature of the PGE, which turns from a siderophile-dominant behaviour in absence of sulphide to a clear chalcophile-dominant behaviour as the melt reach sulphide saturation, means that the PGE content of chromite can thus be used to track the presence of sulphide mineralization (Locmelis et al. in press; Méric et al. 2012).

2 Analytical procedures and sample set

2.1 Analytical procedures and elements

The major elements Cr_2O_3, Al_2O_3, FeO, MgO (Fig. 1), and some minor ones, TiO_2 and V_2O_3, were analysed with an electron microprobe at Université Laval (details in Pagé and Barnes 2009). The data obtained by EMPA are necessary because Fe is used as the internal standard for the LA-ICP-MS analysis, but also to compare EMPA and LA-ICP-MS which give similar results. The LA-ICP-MS analytical procedures for Mg, Al, Si, S, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Cu, Ge, As, Y, Mo, Ag, Cd, In, Sn, Sb, W, Re, Au, Pb in chromite are very similar to those for magnetite presented in Dare et al. (2012) and to Pagé et al. (2012) for PGE.

The new results presented here have been obtained with our recent laser ablation system (M-50 resolution Excimer:193nm from Resonetics) combined with a new ICP-MS (x7700 from Agilent).

2.2 Sample set

Analyses were conducted on chromites from a wide range of samples (Fig. 1) representative of various volcanic settings: MORB, boninites, komatiites, continental flood basalt (CFB picrite) and from various

plutonic settings: mantle podiform chromitites from Thetford Mines Ophiolite (TMO), crustal stratiform chromitites from Stillwater Complex.
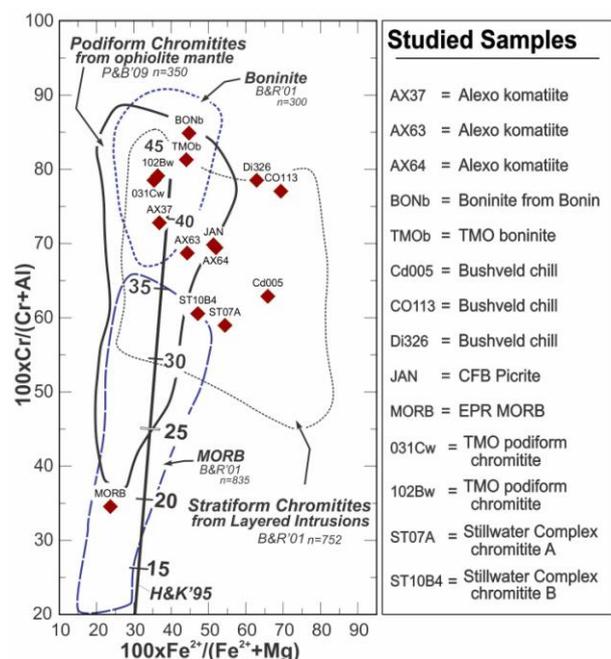

Figure 1. Major element composition of chromite from the studied samples compared to the fields of chromite from podiform chromitites (Pagé and Barnes 2009), from stratiform chromitites, from boninites and from MORB (Barnes and Roeder 2001). They are also compared to a batch melting trend from Hirose and Kawamoto (1995).

3 Results and discussion

3.1 Trace elements and PGE by LA-ICP-MS

A wide range of elements have been analysed by LA-ICP-MS in addition to the major and minor elements and the PGE. Here we focus on Os, Ir, Ru and Rh which have been determined in chromite at concentrations ranging from below detection levels (1-6 ppb) up to ~440 ppb. In certain cases the PGE are clearly present in solid solution in the chromite, and can even be accompanied by PGM, sulphide and silicate inclusions (Fig. 2).

The Os and Ir concentrations (7-69 ppb and 4-46 ppb, respectively) show a strong positive correlation (Fig. 3a), and they also correlate positively with Fe, Ga (*not shown*) and Ni (Fig. 3d), but negatively with Mg. This suggests that Os and Ir behave the same way as Ni, i.e. they prefer the octahedral coordination site, and may be influenced by the proportion of oxidized Fe (Brenan et al. 2012).

The most abundant PGE in chromite is Ru which varies between 20-450 ppb (Fig. 3b) and Rh which ranges from 4-61 ppb (Fig. 3c), they both show a weak positive correlation with Ir. In terms of Ru our samples are forming two distinctive groups: one has low Ru content (20-100 ppb) and the other with higher concentrations ranging from 200-440 ppb (Fig. 3b). Ruthenium shows a stronger positive correlation (*not shown*) with Rh. However, Ru and Rh do not show any correlation with Ni.
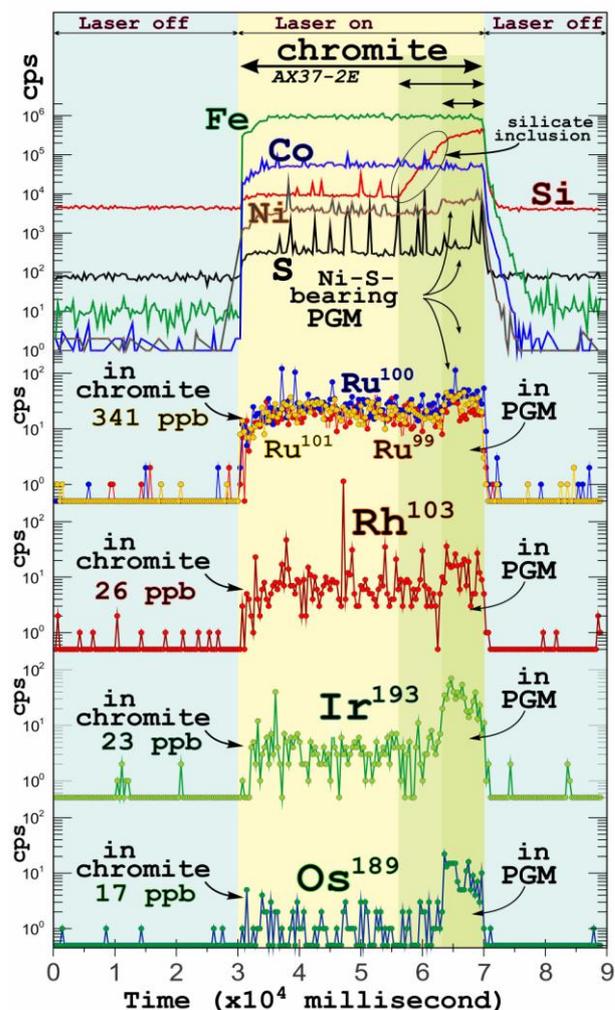

Figure 2. LA-ICP-MS analysis of a chromite from Alexo komatiites showing the profiles for Fe, Co, Si, Ni, S, Ru^{99}, Ru^{100}, Ru^{101}, Rh^{103}, Ir^{193} and Os^{189} with time. The PGE are both in solid solution in chromite and as PGM inclusions.
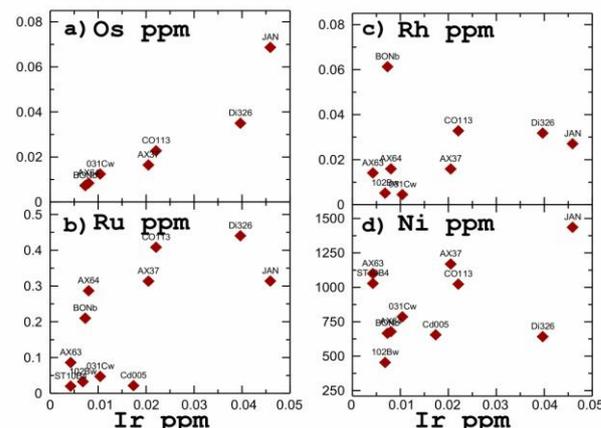

Figure 3. Iridium (ppm) content of chromite against a) Os ppm, b) Ru ppm, c) Rh ppm, and d) Ni ppm.

On the primitive mantle normalized (PM$_N$) PGE profiles of chromites, we observe a clear enrichment in Ru relative to Os and Ir, which show similar and essentially flat PGE profiles with concentrations from 2x to 20x the primitive mantle values (Figs 4 and 5). On the PM$_N$ PGE profiles of chromite, Ru often defines a positive anomaly with concentrations ranging from 2x

to 90x the primitive mantle values. The lowest concentrations of Ru have been measured in chromite from chromitites in plutonic settings (podiform and stratiform; Fig. 5a) containing abundant PGM such as laurite. The highest concentrations of Ru have been obtained from chromite from volcanic settings, i.e. from the CFB picrite and komatiites, and to a lesser extent from boninites (Fig. 4).
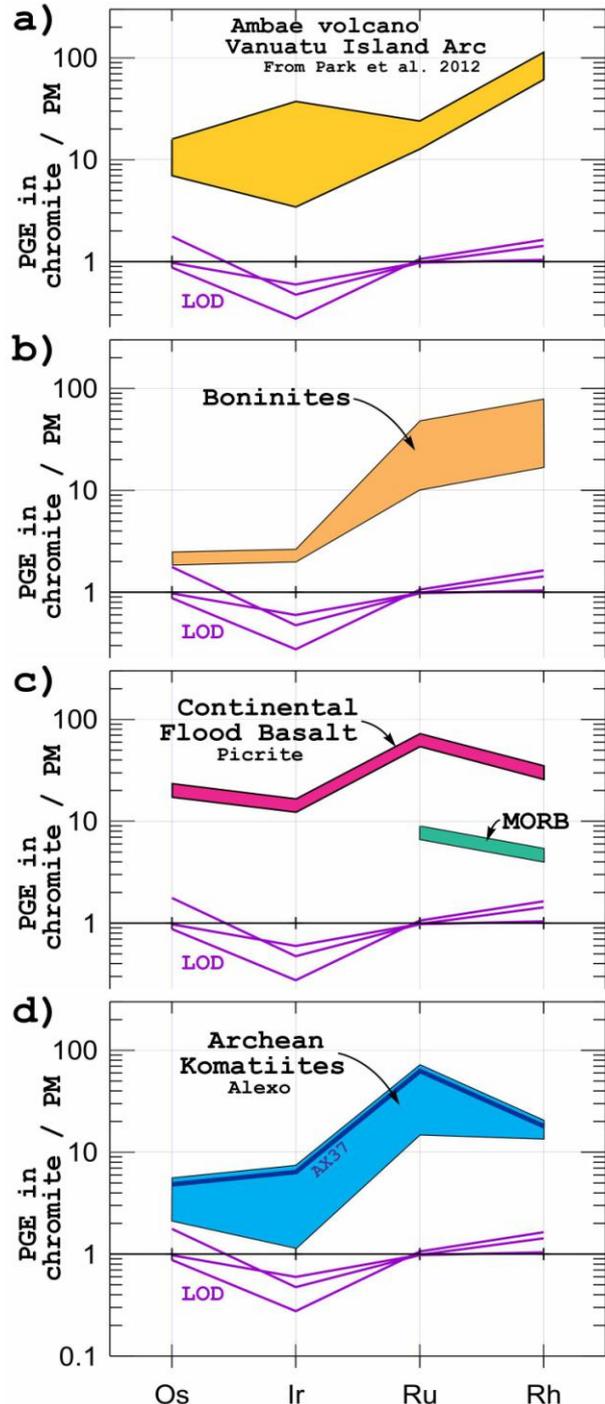
The high Ru_N/Ir_N ratios correlate with Rh content suggesting that Rh and Ru are preferentially concentrated into chromite relative to Ir (and Os). Most of the PM_N PGE profiles of chromite show $Ru_N > Rh_N$, with the exception of the chromite from boninites and the Ambae volcano which tend to show $Ru_N < Rh_N$ (Fig. 4a, b), a particularity that could characterize oxidized volcanic arc magmas.
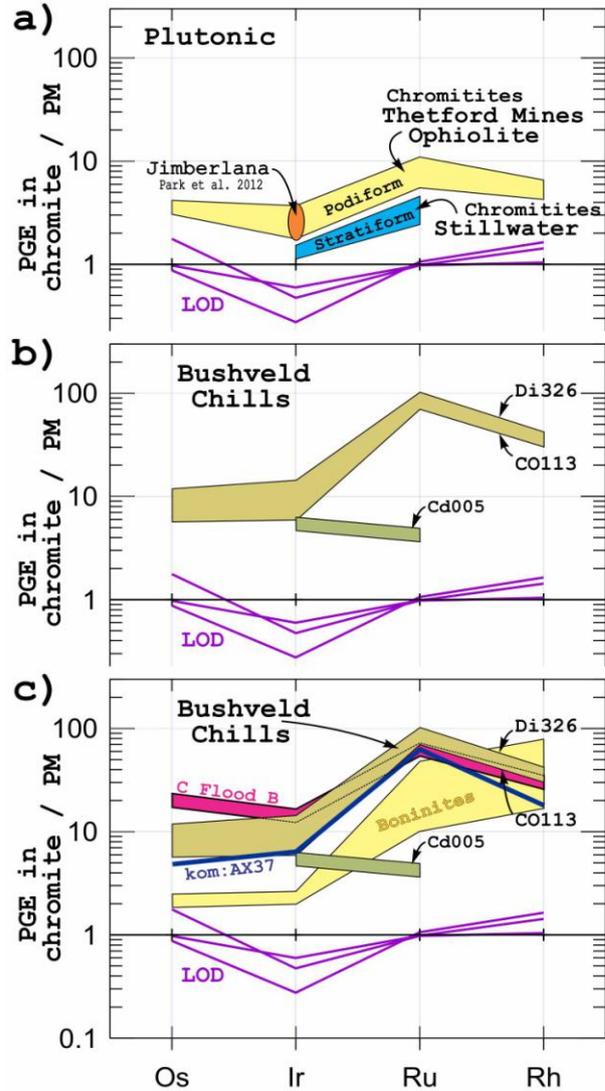

Figure 4. Primitive mantle normalized PGE profiles for chromite from volcanic settings; a) Ambae island arc volcano (data are from Park et al. 2012), b) Boninites, c) Continental flood basalt and a MORB sample, d) Komatiites. Normalizing values (in ppb) are Os=3.4; Ir=3.2; Ru=5.0; Rh=0.9; and are from Lyubetskaya and Korenaga (2007). LOD = Limit of detection.

Figure 5. Primitive mantle normalized PGE profiles for chromite from plutonic settings; a) Mantle podiform, crustal stratiform chromitites, b) the chills of the Bushveld Complex, and c) the chills of the Bushveld are compared with chromite from possible parental magmas (continental flood basalt, komatiites and boninites).

On Figure 4, chromites from the various lava samples show distinctive PGE profile that can tentatively be used to identify the nature of the melt from which these chromites have crystallized. In Figure 5c, chromites from the chills of the Bushveld Complex are compared to chromite from potential parental magmas such as continental flood basalt, komatiite and boninite. Chromites from Cd005 sample are clearly different from chromites from the two other samples (Di326 and CO113). When compared with the chromite from the other lava samples, the Bushveld chill chromite most

closely resembles chromite from the continental flood basalt and komatiites, with higher Os and Ir contents, and similar Rh_N/Ru_N of ~0.4-0.5. There is a clear difference between the chromite from boninite and the chromite from the chills of the Bushveld Complex (Fig. 5c).

3.3 The role of chromite on the PGE budget and $D_{PGE}^{Chr/melt}$

Similarly to Pagé et al. (2012) who evaluated the role of chromite on the whole rock PGE budget, the results from this analysis are summarized in Table 1.

Table 1. Proportion of whole rock PGE accounted for by the chromite from the different lithologies.

Name	Litho	%WR-Os in Chr	%WR-Ir in Chr	%WR-Ru in Chr	%WR-Rh in Chr
AX37	komatiite	18%	25%	~100%	38%
MORB	MORB	<26%	<13%	93%	76%
BONb	boninite	88%	>100%	77%	30%
TMOb	boninite	<5%	<5%	45%	11%
JAN	CFB-picrite	10%	9%	35%	14%

New partition coefficients for Os, Ir, Ru and Rh between chromite and various melts have been calculated (Table 2) following the method of Pagé et al. (2012).

Table 2. Partition coefficients for chromite and various melts.

Name	Litho	$D_{Os}^{Chr/melt}$	$D_{Ir}^{Chr/melt}$	$D_{Ru}^{Chr/melt}$	$D_{Rh}^{Chr/melt}$
AX37	komatiite	9.7	14	60	20
MORB	MORB	<37	<18	129	105
BONb	boninite	183	365	159	61
TMOb	boninite	<14	<13	125	31
JAN	CFB-picrite	40	36	139	56

4 Conclusions

Chromite acts as a sink for the PGE, not only because it can entrap PGM during their crystallization, but also because Os, Ir, Ru and Rh partition into chromite structure. The highest concentration has been measured for Ru reaching ~300 ppb in the chromites from continental flood basalt and komatiites, and as high as 440 ppb in the chromite from the Bushveld chills. Chromites from komatiites, flood basalt, podiform chromitites, and from the Bushveld chills show Rh_N/Ru_N of <1, opposite to chromites from boninites and from Ambae arc lavas (Rh_N/Ru_N>1), which seems to be typical of oxidized arc magmas.

The PGE normalized profiles of chromite can thus be used to characterize the nature of the melt from which the chromite has crystallized. The whole rock data combined with the PGE content of chromites allowed us to present new partition coefficients.

Acknowledgements

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