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Geochemical composition of chromite from Alexo komatiite in the western Abitibi greenstone belt: Implications for mineral exploration

Philippe Pagé¹, Sarah-Jane Barnes¹, Julien Méric¹, and Michel G. Houlé²

¹Université du Québec à Chicoutimi, Saguenay, Quebec

²Geological Survey of Canada, Québec, Quebec

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Contribution to the Geological Survey of Canada's Targeted Geoscience Initiative 4 (TGI-4) Program (2010–2015)

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Geochemical composition of chromite from Alexo komatiite in the western Abitibi greenstone belt: implications for mineral exploration

Philippe Pagé^{1*}, Sarah-Jane Barnes¹, Julien Méric¹, and Michel G. Houlié²

¹Canada Research Chair in Magmatic Ore Deposits, D.S.A. Sciences de la Terre, 555, boulevard de l'Université, Université du Québec à Chicoutimi, Saguenay, Quebec G7H 2B1

²Geological Survey of Canada, 490 rue de la Couronne, Québec, Quebec G1K 9A9

*Corresponding author's e-mail: Philippe_Page@uqac.ca

ABSTRACT

This study, which focuses on the composition of chromite from mineralized and unmineralized komatiitic flows and sills from the Alexo Mine area in Dundonald Township, within the western Abitibi greenstone belt, aims to develop new exploration tools for poorly exposed mineralized komatiitic systems. It is possible to clearly identify chromite derived from massive sulphide (having very high Cr# and depleted Ru content) from chromite derived from barren and poorly mineralized samples based on its composition. LA-ICP-MS analyses show that chromite from massive sulphide are depleted in Al, Ni, and Mg, and are enriched in Ti, Zn, Mn, Fe and V compared to chromite from barren samples; however, alteration can also modify chromite chemistry. Samples from the Hart deposit are pervasively altered and their chromite compositions are enriched in Fe, Zn, Co, and Mn, and are depleted in Mg. We propose a binary diagram of Ni/Mn versus Ni/Cr ratios which can be used to clearly discriminate between sulphide segregation prior to chromite crystallization and later superimposed alteration. Mass balance calculations show that chromite does fractionate and concentrate Ir-group platinum-group elements (IPGE: Os, Ir, Ru) and Rh but that chromite contribution to the whole-rock IPGE and Rh budget is rather limited, and for mineralized samples, this contribution is even smaller. From these results, it is clear that IPGE+Rh-rich phases (nano- to micro- platinum-group minerals) are needed to account for the IPGE and Rh contents in whole-rock geochemistry.

INTRODUCTION

This study, part of the Targeted Geoscience Initiative 4 (TGI-4) program, focuses on the chromite composition from mineralized and unmineralized komatiitic flows and sills at the Alexo Mine area in Dundonald Township, within the western Abitibi greenstone belt (WAGB). There were several goals of the present work. (1) Develop a method to use chromite as an indicator mineral for ore-forming processes related to Ni-Cu-(PGE) mineralization associated with komatiite. (2) Explore whether chromite composition can be used to constrain magmatic to post-magmatic processes involved in the generation and the evolution of komatiitic rocks, such as the order of crystallization, sulphide segregation, metamorphism, and alteration. (3) Define a typical signature associated with Ni-Cu-(PGE) sulphide mineralization that can be used targeting prospective regions in exploration campaigns within poorly exposed and/or extensively overburden-covered areas.

Experimental studies of sulphide-undersaturated melts have suggested that chromium-rich spinel frac-

tionates platinum-group elements (PGE) and preferentially incorporates osmium, iridium, ruthenium, and rhodium, which are found to be compatible; platinum and palladium stay in the magma during fractional crystallization as they are incompatible in chromite (e.g. Righter et al., 2004; Brenan et al., 2012). Recently, Locmelis et al. (2011, 2013), Pagé et al. (2012), Park et al. (2012) and Arguin et al. (2014) demonstrated from natural samples that ruthenium in particular, but also osmium, iridium, and rhodium, are incorporated into chromite in the absence of an immiscible sulphide melt, and are, on the other hand, expected to partition into sulphide when droplets of sulphide liquid are present (Fig. 1). Therefore, it has been suggested that a better understanding of Ir-group platinum-group elements (IPGE: Os, Ir, Ru) and Rh behaviour during chromite crystallization in komatiitic systems might lead to new exploration tools (i.e. IPGE+Rh-rich chromite = barren komatiite while IPGE+Rh-poor chromite = mineralized komatiite) that could vector toward Ni-Cu-(PGE) sulphide mineralization in komatiitic systems.

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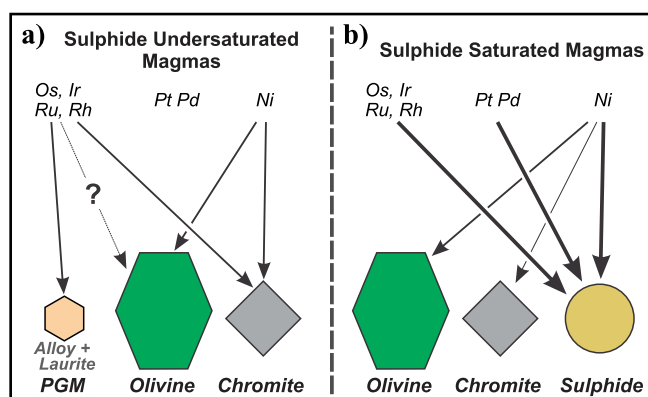


Figure 1. Illustration showing the behaviour of Ir-group platinum-group elements (Os, Ir, Ru) and Rh during the crystallization of (a) sulphide-undersaturated magma and (b) sulphide-saturated magma. Abbreviations: PGM = platinum-group minerals.

METHODOLOGY

Sample Selection

Samples used in this study must meet three criteria: i) low metamorphic grade (prehnite-pumpellyite up to lower greenschist metamorphic facies; Arndt, 1986), ii) well preserved primary volcanic textures and structures with localized and non-penetrative deformation (Houlé et al., 2012), and iii) large number of samples must be available from a well characterized geological setting. A suite of 47 well preserved samples, which many contains relics of olivine, from the Alexo Mine area were selected as they had been well described by Barnes (1983) and Houlé (2008) in their Ph.D. studies (24 samples from Barnes (1983); 23 samples from Houlé (2008)). Another 6 samples were selected to investigate the effect of alteration on the composition of komatiitic chromite from the komatiite-associated Ni-Cu-(PGE) Hart deposit in the Shaw Dome area in the WAGB, which is pervasively serpentinized and affected by talc-carbonate alteration. The reader is also referred to Barnes et al. (1983), Houlé et al. (2012), and Méric et al. (2012) for detailed geology of the study area.

Analytical Methods

Detailed petrographic work has been conducted on the selected samples to characterize their mineralogy, texture, and degree of alteration. Chromite grains selected were subsequently analyzed with the electron microprobe at Laval University and the LA-ICP-MS at Université du Québec à Chicoutimi. Samples were also analyzed for whole-rock and PGE geochemistry. Detailed analytical parameters and procedures will be presented in a forthcoming dissertation by J. Méric.

RESULTS

Chromite Chemistry

The composition of chromite from the Alexo Mine and

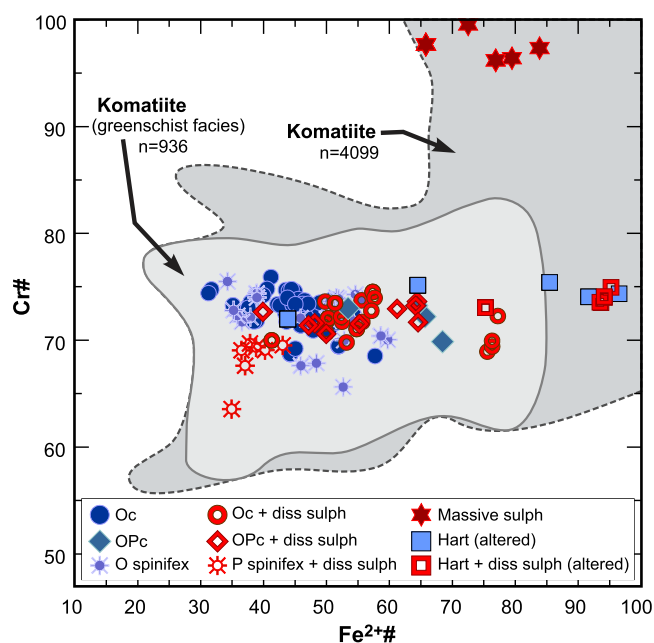


Figure 2. Cr# ($100\text{Cr}/(\text{Cr}+\text{Al})$) versus $\text{Fe}^{2+\#}$ ($100\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$) diagram of chromite from komatiite from the Alexo Mine area and the Hart deposit. Fields are compiled from Barnes and Roeder (2001). Medium-grey field outlines the composition of chromite in komatiite of various facies, metamorphic grades, and alteration degrees; light-grey field outlines the composition of chromite from komatiite that has undergone greenschist or lower grade metamorphism. Abbreviations: Oc = olivine cumulate; OPc = olivine + pyroxene cumulate; O spinifex = olivine spinifex; diss sulph = disseminated sulphide; P spinifex = pyroxene spinifex; sulph = sulphide.

Hart deposit plot in a limited range of Cr# ($100\text{Cr}/(\text{Cr}+\text{Al})$), from ~ 65 to ~ 75 , but exhibit a much wider range of $\text{Fe}^{2+\#}$ ($100\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$), from ~ 35 to ~ 75 at Alexo Mine and from ~ 45 to ~ 95 at Hart deposit (Fig. 2). However, a group of chromite from massive sulphide samples from Alexo exhibits a very distinctive chemistry with very high Cr# (~ 97.5) and a range of $\text{Fe}^{2+\#}$ from ~ 66 to ~ 84 (Fig. 2). The distinction between barren samples and those containing traces of disseminated sulphides is not clearly defined based on major elements, even though the latter tend to have higher $\text{Fe}^{2+\#}$. However, results of trace elements obtained from LA-ICP-MS do show significant differences between mineralized and barren samples (Fig. 3). Chromite from olivine cumulates and olivine-spinifex samples have very similar patterns, which are representative of typical signatures of well preserved and unmineralized samples (Fig. 3). Compared to these samples, chromite from the sulphide-rich samples are enriched in Ti, Mn, FeO^* , and V, and are depleted in Al_2O_3 , Ni, and MgO (Fig. 3a). To explore alteration effects, chromite from highly altered samples of the Hart deposit was also compared to the chromite from the fresh and unmineralized olivine cumulates and olivine-spinifex komatiite samples (Fig. 3b). The

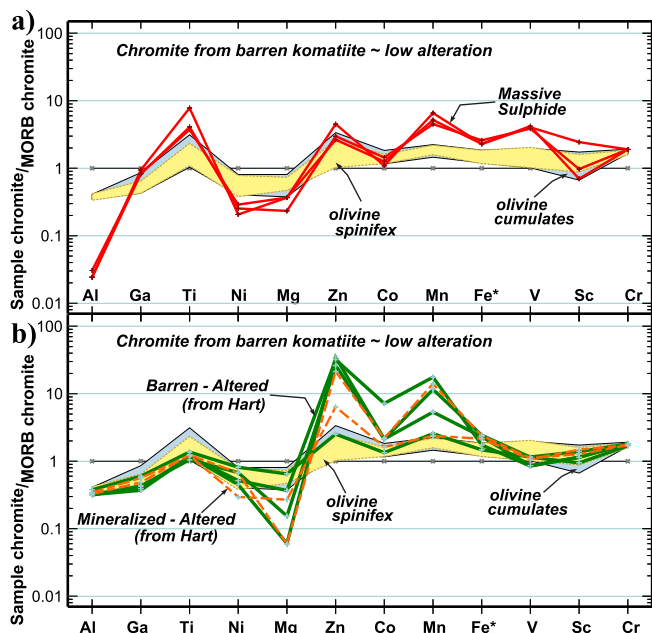


Figure 3. Multi-element profiles of chromite from barren olivine cumulates and olivine-spinifex compared to chromite from (a) massive sulphide samples and from (b) pervasively altered samples from the Hart deposit. Normalized to the composition of chromite in mid-ocean ridge basalt (MORB) from Pagé and Barnes (2009).

mobility of some element during alteration is strongly supported on this diagram by an increase in Zn, Co, Mn, and a decrease in Mg contents (Fig. 3b). However, the alteration seems to have little effect on elements having higher valencies ($\geq 3+$), with the possible exception of Fe^{3+} . Based on these observations, elemental ratios were identified to that would distinguish between the main magmatic processes (e.g. fractional crystallization versus sulphide segregation), and also evaluate alteration effects (Fig. 4). The plot of Ni/Ti ratios versus Ni/Cr ratios illustrates the combined effect of fractional crystallization and possible sulphide segregation on the chromite composition during the evolution of the komatiitic magma (Fig. 4a). These two ratios do not appeared to be greatly influenced by alteration. Other processes are discernible by plotting Ni/Mn versus Ni/Cr ratios (Fig. 4b): (1) alteration processes are suggested by a decrease in the Ni/Mn ratio (very low values because of high Mn content), and (2) the presence of sulphide phases in the paragenesis are indicated by the change in the slope at Ni/Mn < 0.4 (Fig. 4b).

Osmium, Iridium, Ruthenium, and Rhodium in Chromite

Ruthenium has the highest concentrations of the IPGE and Rh, ranging from <10 to 450 ppb (Fig. 5); Os, Ir, and Rh have a more limited range of <1–5 to 75 ppb (not shown). Despite the very high affinities of IPGE and Rh for sulphides compared to chromite ($D_{sulph/melt}$

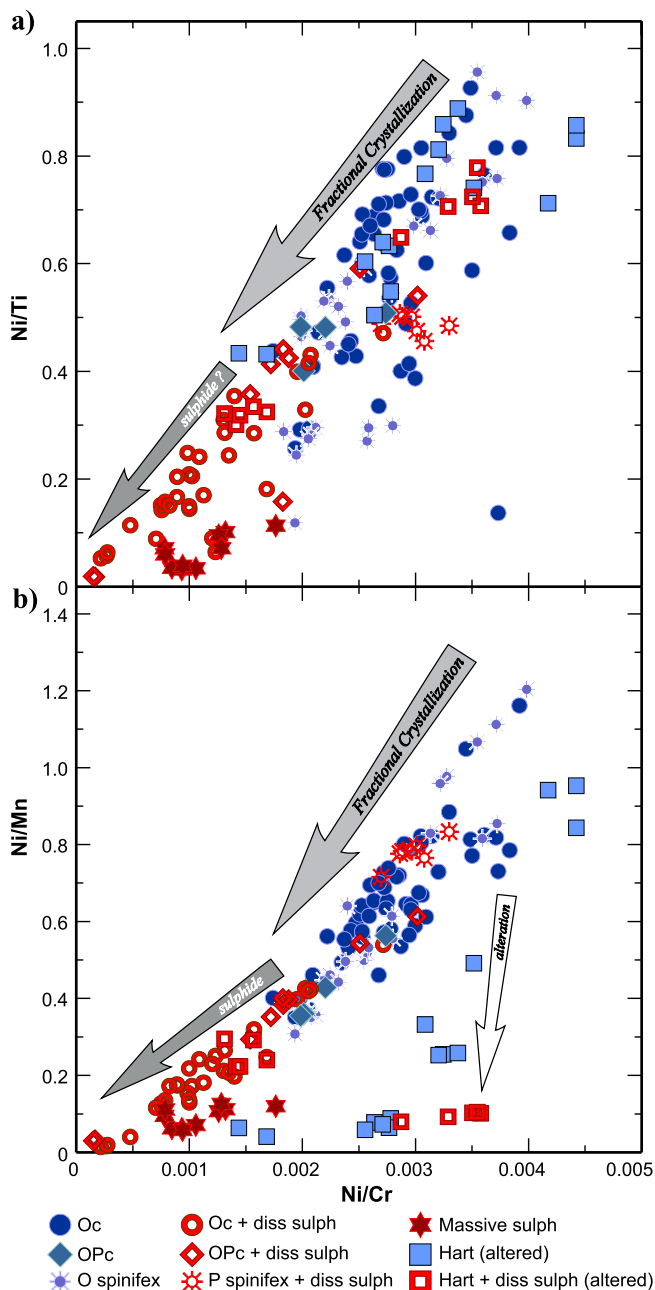


Figure 4. Binary plots of metal ratios (a) Ni/Ti versus Ni/Cr and (b) Ni/Mn versus Ni/Cr for chromite from komatiite from the Alexo Mine area and the Hart deposit. Abbreviations: Oc = olivine cumulate; OPc = olivine + pyroxene cumulate; O spinifex = olivine spinifex; diss sulph = disseminated sulphide; P spinifex = pyroxene spinifex; sulph = sulphide.

$/ D_{chr/melt} \approx 1000$), the data presented here for Ru cannot be readily interpreted as Locmelis et al. (2013) proposed. These authors concluded that the presence of Ru-rich chromite indicates a barren system and conversely that Ru-poor chromite indicates a mineralized system. From the distribution observed in Figure 5, chromite that crystallized from sulphide liquid is effectively depleted in IPGE and Rh and chromite from barren samples usually contain >150 ppb Ru. However, it

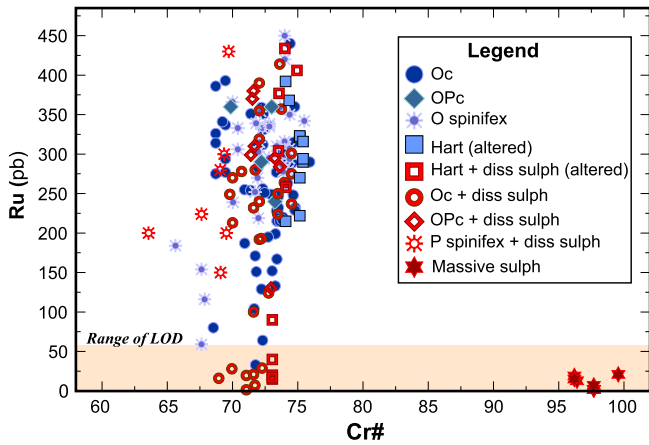


Figure 5. Diagram showing the concentration of Ru in chromite versus its Cr# ($100Cr/(Cr+Al)$). Chromite is from komatiites from the Alexo Mine area and the Hart deposit. Abbreviations: Oc = olivine cumulate; OPc = olivine + pyroxene cumulate; O spinifex = olivine spinifex; diss sulph = disseminated sulphide; P spinifex = pyroxene spinifex; sulph = sulphide.

is not as clear for sulphide-bearing samples as these cover the entire range of Ru concentrations, with a group of depleted chromite, which is expected when sulphide segregates before chromite crystallization (Fig. 5). These observations strongly suggest that the timing of chromite crystallization versus sulphide segregation is a critical factor to consider during interpretation of the results.

To constrain the effects of sulphides and, if possible alteration, a primitive mantle normalized (PM_N) profile was generated to compare the IPGE and Rh contents of chromite from samples of sulphide-bearing (disseminated to massive) and from the Hart deposit with chromite from samples of fresh and barren olivine cumulate and olivine-spinifex from the Alexo Mine (Fig. 6, see also Table 1). Chromite from the barren Alexo komatiite has PM_N IPGE and Rh profiles enriched in all four elements, a positive Ru anomaly

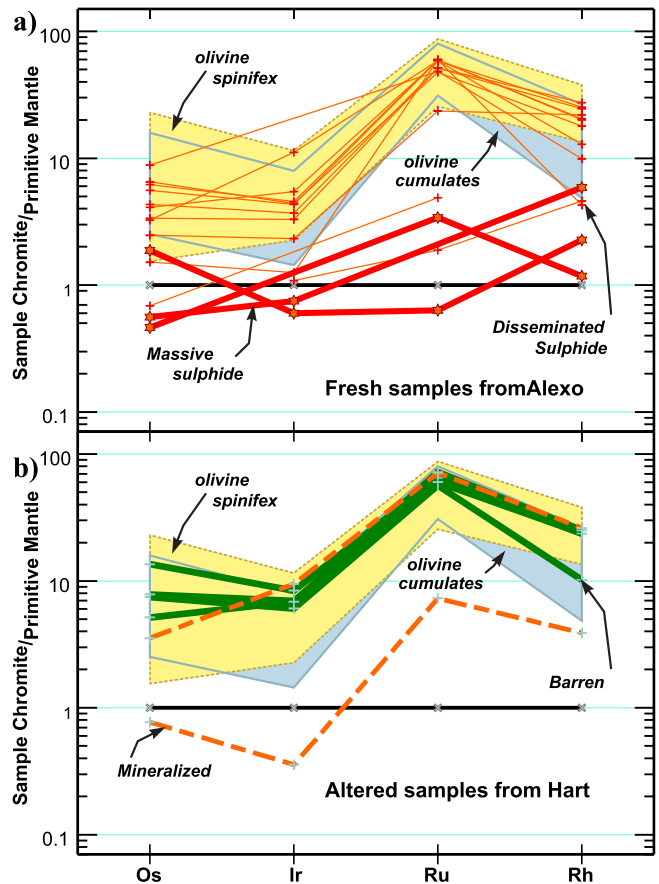


Figure 6. Primitive mantle normalized Ir-group platinum-group elements (Os, Ir, Ru) and Rh profiles for chromite from olivine cumulates and olivine-spinifex compared to chromite from (a) the sulphide-bearing samples, and (b) the pervasively altered Hart deposit samples. Normalizing values are from McDonough and Sun (1995).

($Ru_N/Ir_N \sim 14 - 15$; $Ru_N/Rh_N \sim 3 - 4$), and displays no significant differences between chromite from samples of olivine cumulate or spinifex. When compared to chromite from the sulphide-bearing samples, the first thing to note is the depleted PM_N IPGE and Rh profiles

Table 1. Osmium, iridium, ruthenium, and rhodium content of chromite.

	Os (ppb)			Ir (ppb)			Ru (ppb)			Rh (ppb)		
	min	avg	max	min	avg	max	min	avg	max	min	avg	max
Alexo Mine Komatiite												
Barren	5.3	20.8	77.5	4.6	14.3	37	128	277	435	4.4	13.9	23.5
mantle value	1.6x	6.1x	22.8x	1.4x	4.5x	11.6x	25.6x	55.5x	87x	4.9x	15.4x	26.1x
Diss. Sulphides	2.33	12.9	30	bdl	10.8	35.6	9.4	217.1	299.2	bdl	15.4	24.6
mantle value	0.7x	3.8x	8.8x	-	3.4x	11.1x	1.9x	43.4x	59.8x	-	17.1x	27.3x
Mass. Sulphides	bdl	3.3	6.35	bdl	~2	2.4	bdl	10.1	17	bdl	2.8	5.3
mantle value	-	1.0x	1.9x	-	0.6x	0.75x	-	2.0x	3.4x	-	3.1x	5.9x
Hart Deposit Komatiite												
Barren	17.5	28.9	46	19.4	22.6	26.8	284	317.9	362.4	9.2	18.6	22.6
mantle value	5.2x	8.5x	13.5x	6.1x	7.1x	8.4x	56.8x	63.6x	72.5x	10.2x	20.6x	25.1x
Diss. Sulphides	2.6	7.3	12	bdl	~12	30.3	36.4	196.1	355.8	3.5	13.5	23.5
mantle value	0.8x	2.2x	3.5x	-	3.8x	9.5x	7.3x	39.2x	71.2x	3.9x	15.0x	26.1

Abbreviations: avg = average; bdl = below detection level; Diss = disseminated; Mass. = massive; max = maximum; min = minimum

Note: (6.1x) = 6.1 times the mantle value

of the chromite from the massive sulphide samples, essentially less than the detection limits. The Os, Ir, and Rh contents of chromite from most of the samples containing sulphides include the range of chromite from barren samples down to the limits of detection. On the other hand, Ru content does not show the same spread; it tends to cluster around $\sim 55\times$ mantle (~ 275 ppb), with only few analyses at lower Ru concentrations (Fig. 6a). Chromite from the Hart deposit is also mostly enriched in all four elements and has a positive Ru anomaly ($Ru_N/Ir_N \sim 8.8$; $Ru_N/Rh_N \sim 3.3$), similar to the enriched part of the fields of chromite from barren Alexo samples (Fig. 6b). The fact that chromites are still enriched in IPGE and Rh despite their pervasive alteration suggests an immobile behaviour of IPGE and Rh until upper greenschist grade, and preservation of IPGE and Rh signatures. One sample from Hart contains IPGE+Rh-poor chromite that probably crystallized from an already sulphide-saturated magma (Fig. 6b).

The LA-ICP-MS results in this study strongly support the presence of IPGE and Rh in solid-solution within chromite, even though its total contribution to the whole-rock IPGE and Rh budgets is unknown. Mass balance calculations have been conducted to investigate the overall contribution of chromite to the whole-rock IPGE and Rh contents using the following formula:

$$F_{Chr}^{PGE} = 100 \times (C_{Chr}^{PGE} \times (C_{WR}^{Cr} / C_{Chr}^{Cr})) / C_{WR}^{PGE} \quad (1)$$

Where:

$$F_{Chr}^{PGE} = \text{whole-rock fraction of IPGE and Rh accounted by chromite}$$

$$C_{Chr}^{PGE} = \text{IPGE and Rh concentration in chromite}$$

$$C_{WR}^{Cr} = \text{Cr}_2\text{O}_3 \text{ concentration in whole rock}$$

$$C_{Chr}^{Cr} = \text{Cr}_2\text{O}_3 \text{ concentration in chromite}$$

$$C_{WR}^{PGE} = \text{IPGE and Rh concentration in whole rock}$$

The results show that chromite does have a real effect on the fractionation and concentration of IPGE and Rh, and that although its contribution to the whole-rock budgets is relatively minor for Os, Ir, and Rh, it is significant for Ru (up to 90% of whole-rock budget, Fig. 7). Indeed, chromite from the barren samples on average account for $\leq 10\%$ of the whole-rock Os, Ir, and Rh budgets, and for 45% of the whole-rock Ru budget, with the exception of 1/5 of the samples in which chromite accounts for $>75\%$ of the whole-rock Ru budget (Fig. 7). For the sulphide-bearing samples, chromite contributes even less to the whole-rock IPGE and Rh budgets; it accounts, on average, for $\leq 5\%$ of the whole-rock Os, Ir, and Rh budgets, and for $\sim 15\%$ of the whole-rock Ru budget, not reaching a contribution of higher than 37%.

DISCUSSION

Our results show that chromite from the Alexo Mine and the Hart deposit have typical komatiitic composi-

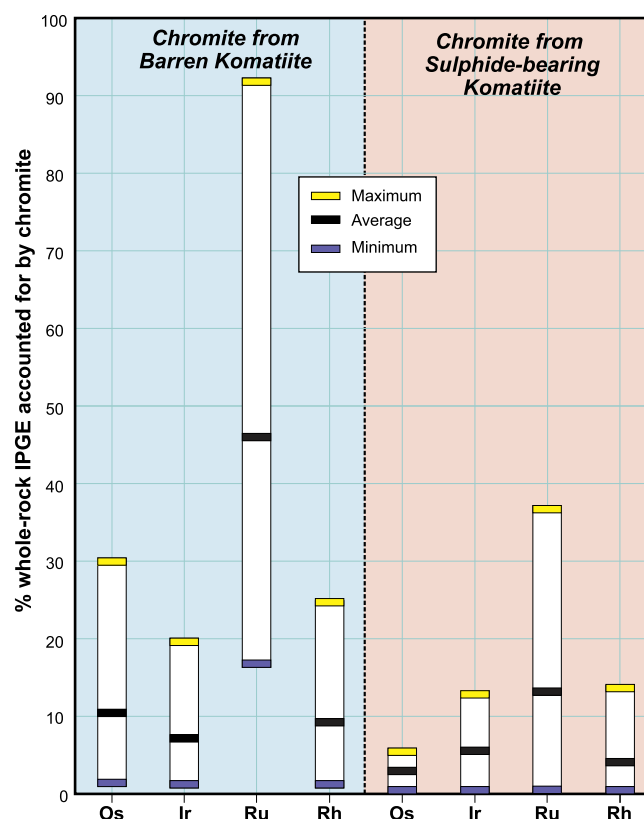


Figure 7. Mass balance calculations showing the contribution of chromite to the whole-rock Ir-group platinum-group elements (Os, Ir, Ru) and Rh budgets for (a) barren komatiite and (b) sulphide-bearing samples.

tion, with limited variations in Cr# but a larger spread of $Fe^{2+\#}$. Some of the variations observed in the $Fe^{2+\#}$ appeared to be related to alteration of the samples. However, it is difficult to adequately discriminate chromite composition based solely on the major elements, with the exception of chromite from massive sulphides, which are easily recognizable as being depleted in Al, resulting in very high Cr# values. Systematic differences in minor element compositions observed in chromite from massive sulphide and highly altered samples, compared to chromite from fresh and barren komatiite samples, allowed us to propose elemental ratios that underline the effects of fractional crystallization and sulphide segregation, but that also underpin alteration. These two diagrams (Ni/Ti versus Ni/Cr and Ni/Mn versus Ni/Cr) are new geochemical tools that can be used to determine the evolution of the komatiitic magma or its degree of alteration. Contrary to our working hypothesis, samples containing IPGE+Rh-rich chromite are not necessary indicative of the absence of trace or disseminated sulphides, as most of these sulphide-bearing samples contained chromite with high concentrations of Ru. However, sulphide-rich samples (i.e. samples of massive sulphide) were found to contain chromite that is highly depleted in IPGE and Rh. These observations highlight the importance of the

timing between chromite and sulphide saturation as a critical factor controlling the IPGE and Rh content of the chromite. In this study, many samples appeared to reach chromite saturation before reaching sulphide saturation. This is supported by the PM_N IPGE and Rh profiles of the chromite from samples containing disseminated sulphides which shows similarities in abundances and shapes with chromite from the fresh and barren komatiite samples. However, a few samples contain chromite that is partly to strongly affected by sulphide segregation, and the PM_N IPGE and Rh profiles for chromite from these samples are similarly depleted in IPGE and Rh as the chromite found in massive sulphide samples. Our results also show that alteration has limited effect on the chromite IPGE and Rh content. Furthermore, mass balance calculations support the knowledge that chromite partitions and concentrates IPGE and Rh, but chromite's total contribution to the whole-rock content is insufficient to account for the overall IPGE and Rh budget, which suggests that even when sulphides are not present, other IPGE+Rh-rich phases are needed to explain the entire IPGE and Rh abundances of whole-rock analysis.

IMPLICATIONS FOR EXPLORATION

It has been proposed by Locmelis et al. (2011, 2013) that the depleted Ru content in chromite is indicative of chromite that crystallized in equilibrium with a sulphide liquid, and that Ru-depleted chromite can be used as an effective exploration tool to vector toward mineralized komatiitic sequences. Despite the fact that in our study, chromite from massive sulphide samples (which were extremely depleted in Ru) strongly support this interpretation, our results from less mineralized samples show the coexistence of chromite with both depleted and enriched Ru content suggesting a more complex evolution of the komatiitic systems. These results are best explained by a mixing of chromite that crystallized from a sulphide-undersaturated magma (Ru-enriched chromite) and a sulphide-saturated magma (Ru-depleted chromite) supporting the flow-through komatiitic system at Alexo as proposed by Houlé et al. (2012). Indeed, the use of metal ratios (Ni/Mn versus Ni/Cr) has allowed us to discriminate barren from mineralized samples, but also to illustrate alteration effects. So far, in terms of chromite composition, it seems that the combination of Ru versus Cr# and Ni/Mn versus Ni/Cr diagrams constitutes good exploration tools for identifying chromite derived from mineralized versus barren lithologies within komatiitic successions. However, further investigations are needed to fully characterize and understand the behaviour of IPGE and Rh in order to use them as a more efficient tool for targeting the most prospective units in komatiitic systems.

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