

46. Geochemistry of Chromite from the Alexo Komatiite, Dundonald Township: Preliminary Results from Electron Microprobe and Laser Ablation Inductively Coupled Plasma Mass Spectrometric Analyses

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INTRODUCTION

Komatiite-associated nickel-copper-platinum group element (PGE) sulphide deposits exhibit generally a relatively small footprint and are becoming more and more difficult to find especially within poorly exposed and extensively overburden covered Archean and Proterozoic greenstone belts. It has been proposed that litho-geochemistry can be used to discriminate between rocks from mineralized and barren environments (e.g., Lesher et al. 2001). However, despite the fact these litho-geochemical indicators can be used as exploration guidelines, Barnes et al. (2004) suggests that, overall, the most reliable indicator of the presence of nickel sulphide mineralization, by far, is the presence of nickel-enriched sulphides.

Experimental studies have suggested some PGE fractionation between chromium-rich spinel and silicate melts where iridium, rhenium and ruthenium are found to be compatible and to be preferentially incorporated into the chromium-rich spinel, whereas palladium and platinum are found to be incompatible and stay in the magma during fractional crystallization (e.g., Righter et al. 2004). More recently, the work of Locmelis et al. (2011, in press) and Pagé et al. (2012) demonstrated from natural samples that PGE, particularly ruthenium, are preferentially incorporated into chromite in the absence of immiscible sulphide melt, and into sulphide when immiscible sulphide melt droplets are present (Figure 46.1). Therefore, it has been suggested that a better understanding of the behaviour of ruthenium in komatiitic systems might lead to some application for the exploration of magmatic nickel sulphide deposits and might be a good indicator for the presence of nickel-copper and PGE sulphide mineralization in those systems.

The main goal of this study, which is part of the high-magnesium ultramafic to mafic system subproject under the Targeted Geoscience Initiative 4 (TGI-4) (*see* Houlé, Lesher and Metsaranta, this volume, Article 42), is to develop the use of chromite as an indicator mineral for ore-forming processes related to nickel-copper-PGE mineralization associated with komatiites. In addition to ruthenium, other chalcophile elements, such as nickel, copper, cobalt, zinc, tin and also osmium and iridium, could be used to predict the presence of sulphide mineralization. Furthermore, the variations of the concentration of chromium, aluminum, iron, magnesium, titanium, nickel, manganese, vanadium, zinc, cobalt, gallium, scandium, osmium, iridium and ruthenium will be addressed in order to constrain different magmatic and secondary processes (i.e., post-cumulate) involved in the generation and the evolution of komatiitic rocks such as:

- magmatic processes: the melting degree of the mantle source, cooling history, fractional crystallization and crystallization sequence, country rock assimilation and sulphide segregation
- secondary processes: sub-solidus re-equilibration, metamorphism and alteration.

*Summary of Field Work and Other Activities 2012,
Ontario Geological Survey, Open File Report 6280, p.46-1 to 46-12.*

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Furthermore, our data set builds on major, minor and traces elements of chromite in komatiitic systems will be also used to define a typical chromite signature associated with nickel-copper-PGE sulphide mineralization, which can be used in studies of detrital chromites within poorly exposed and/or extensively overburden covered areas.

More specifically, in this contribution are presented the preliminary results of electron microprobe and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of chromite from mineralized and unmineralized komatiitic flows or sills from the Alexo Mine area in Dundonald Township within the Abitibi greenstone belt in Ontario.

GEOLOGICAL SETTING

The komatiites of the Alexo Mine area are recognized as one of the classic and well-preserved examples of komatiites associated with a nickel-copper-(PGE) deposit not only in the Abitibi greenstone belt, but also worldwide. The Alexo Mine is hosted within a volcano-sedimentary succession recognized as the 2720–2710 Ma volcanic episode (e.g., Thurston et al. 2008) located in the northeastern part of Dundonald Township, approximately 45 km northeast of the City of Timmins. This volcanic episode has been subdivided into 3 informal formations by Houlé et al. (2008), which are, from oldest to youngest, 1) the McIntosh Lake formation, 2) the Dundonald formation and 3) the Frederick House Lake formation (Figures 46.2 and 46.3).

The Dundonald formation is composed of felsic volcanoclastic rocks, sulphidic-graphitic argillites, and komatiitic sills and flows. The komatiitic units of the Dundonald formation are subdivided into 4 informal members (oldest to youngest): 1) the Foundation member, 2) the Empire member, 3) the Dundonald South member and 4) the Alexo member (Houlé et al. 2008; *see* Figure 46.3). Iron-nickel-copper sulphide mineralization occurs at or near the base of all 4 komatiite members, but only those from the Alexo member (Alexo Mine) and the Foundation member (Kelex deposit) have been mined.

More specific to this project, samples investigated through this study are located within i) the Empire member (Small Pit area) that corresponds to a 100 m thick massive komatiitic peridotite sill; ii) the upper part of Dundonald South member, which is represented by thin well-differentiated (i.e., spinifex-textured and cumulate-textured zones) komatiitic flows with hyaloclastite top-flow breccias (described in detail by Barnes, Gorton and Naldrett (1983) and Arndt (1986)); and iii) the Alexo member (Alexo Mine zone) that comprises thick, poorly differentiated olivine orthocumulate to mesocumulate komatiitic flows (Houlé et al. 2008; Houlé, Leshner and Davis 2012).

Mineralized Komatiite

Unmineralized Komatiite

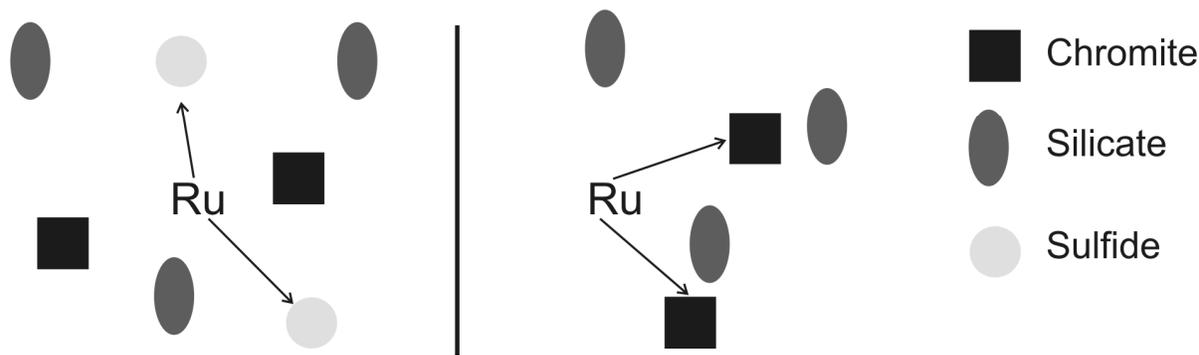


Figure 46.1. Cartoon showing the behaviour of ruthenium in a komatiitic magma where the ruthenium is incorporated within sulphide phases in a sulphide-rich system (left) and incorporated within chromite in sulphide-poor system (right).

METHODOLOGY

Sample Selection

Initially, the komatiite-associated nickel-copper-(PGE) Hart deposit in the Shaw Dome area of the Abitibi greenstone belt, was targeted as a good site for this study, similar to the ongoing companion study on multiple sulphur isotopes also at this site (*see* Hiebert et al., this volume, Article 45). However, preliminary petrographic investigation conducted on samples from the Hart deposit showed that chromites were absent from most of the selected samples and they were also locally pervasively serpentinized, which could have altered the primary geochemical signature of the chromite. As an alternative, the Alexo Mine area was finally selected as the new locality; this was justified by several factors: i) the komatiites are at the prehnite-pumpellyite up to lower greenschist metamorphic facies (Arndt 1986), ii) the deformation is non-penetrative, iii) the primary volcanic textures and structures are very well preserved and, finally, iv) a large suite of samples were available in a well-characterized geological setting. All

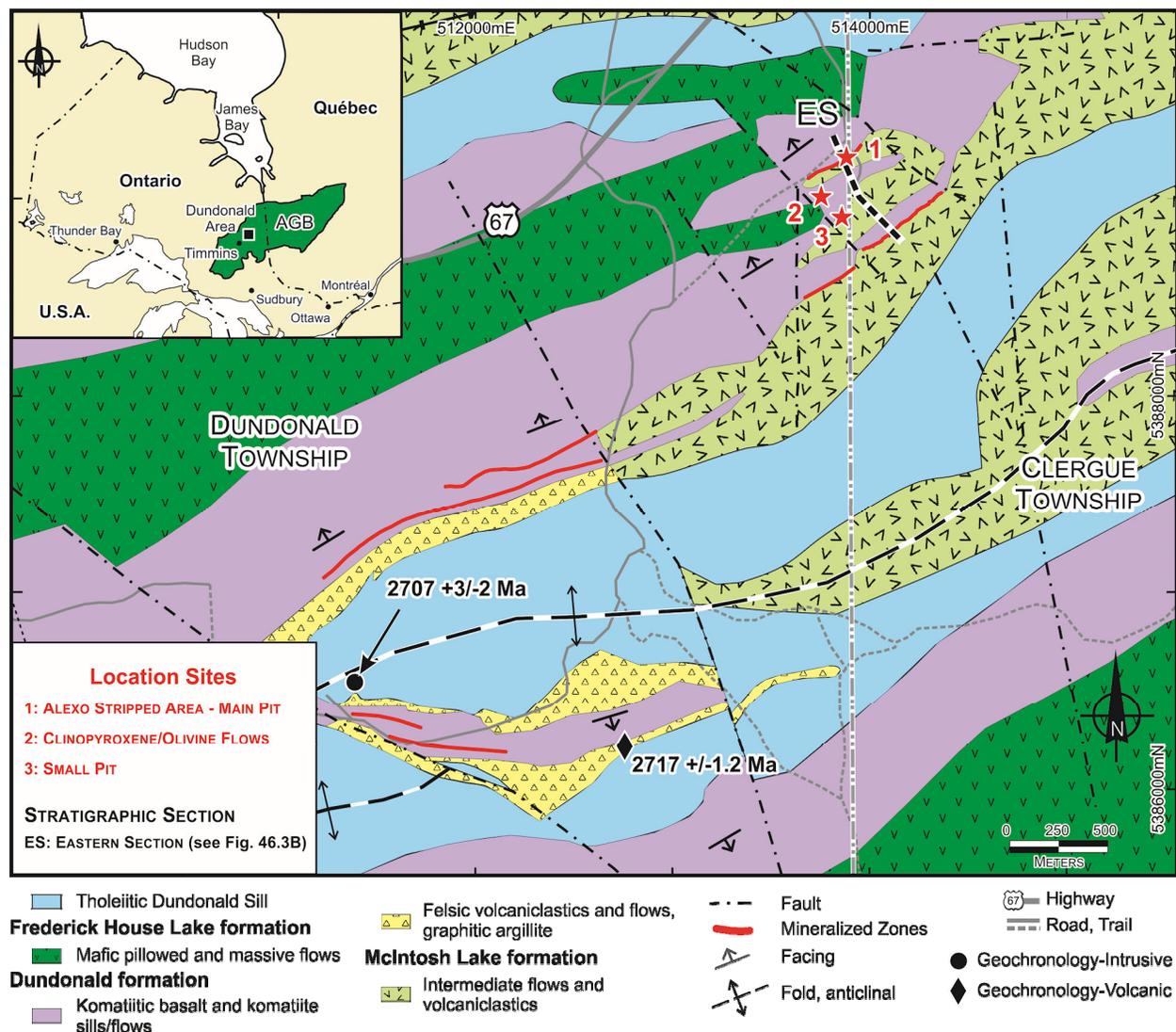


Figure 46.2. Simplified geological map of the Dundonald Township area, Abitibi greenstone belt (AGB), showing major geological units and location sites for this study (*adapted from* Houllé, Leshner and Davis 2012). Section ES (Eastern Section: Alexo Mine) is the location of the stratigraphic column in Figure 46.3B.

these considerations led us to use pre-metamorphic igneous and volcanic nomenclature as rock names in the course of this study. The impact of metamorphism on trace elements content of chromite is not well constrained in comparison to major and minor elements (Barnes 2000). Thus, the low metamorphic grade of the samples (1/3 of the thin sections contain fresh olivine relicts) enhanced the quality and the confidence over the actual and future results on the chromite chemistry. A total of 47 samples have been

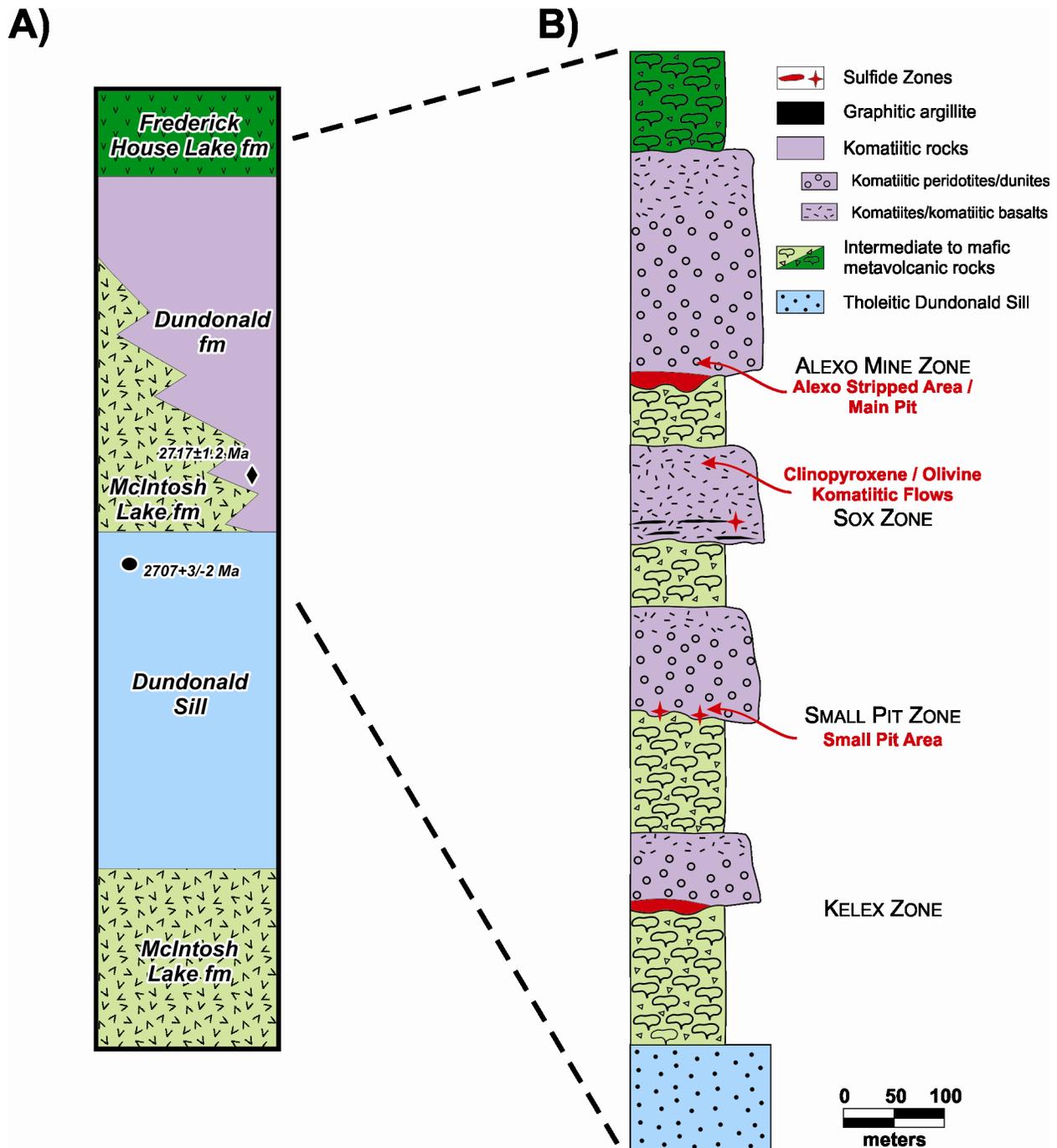


Figure 46.3. A) General schematic stratigraphic column of Dundonald Township (after Houlié et al. 2008). B) Schematic stratigraphy of the Dundonald formation at the Alexo Mine, showing the locations of komatiite-associated nickel-copper-(PGE) deposits or occurrences and location sites for this study (adapted from Houlié, Leshar and Davis 2012).

selected, all from 2 previous studies conducted at the Alexo Mine area, and are allocated as follows: 24 samples are from the PhD thesis of Dr. S.-J. Barnes (Barnes 1983), and 23 samples are from the PhD thesis of Dr. M.G. Houlé (Houlé 2008). At each location, samples were selected along a stratigraphic transect from the basal mineralization up to the olivine cumulate higher up-section, but also laterally to investigate the influence of the proximity of the mineralization.

In this investigation, all samples were grouped into 2 unit-types: the mineralized komatiitic units (i.e., flows and/or sills) and the barren or unmineralized komatiitic units. As an initial attempt, each sample was assigned into one of the unit-types (or groups) based on their actual stratigraphic location. Samples from the Alexo member (Alexo stripped area: 23 samples; and the Main Pit area: 5 samples) and the Empire member (Small Pit area: 6 samples) were assigned to the mineralized komatiitic units and the samples from the upper section of the Dundonald South member (clinopyroxene and olivine komatiitic flows: 13 samples) were assigned to the unmineralized komatiitic units (*see* Figure 46.3). However, the confidence in this preliminary classification scheme is unknown thus far; despite the fact that the samples from the clinopyroxene and the olivine komatiitic flows are known to be unmineralized, some nickel-copper-(PGE) sulphide mineralization is recognized farther to the east and to the west (e.g., Sox zone; Houlé, Leshner and Davis 2012).

Analytical and Laboratory Work

The methodology of the project consists of 4 different and complementary approaches to characterize the chromite geochemistry within mineralized and unmineralized komatiitic units:

- selection of the samples according to their position relative to the mineralization, their facies (cumulate, spinifex, net-textured sulphide, etc.) and the size of chromite (large enough to be analyzed by LA-ICP-MS);
- classic petrographic study with emphasis on the characterization of the chromite morphology, size, texture, alteration and its relation with the other phases that coexist with them;
- electron microprobe analyses of chromite at Laval University (Québec) to determine their major elements content; LA-ICP-MS at Laboratoire des Matériaux Terrestres de l'UQAC (LabMaTer, Saguenay) to determine the minor and trace element and PGE content of chromite;
- whole rock analyses for major and trace elements and PGE content to perform mass balance calculations to determine which elements are influenced by the chromite and sulphide crystallization. Major element analyses, trace element analyses, and PGE analyses were carried out at Activation Laboratories Ltd. (ActLabs, Ancaster), at the Geosciences Laboratories (Geo Labs, Sudbury), and at Laboratoire des Matériaux Terrestres de l'UQAC (LabMaTer, Saguenay), respectively.

PRELIMINARY RESULTS

Petrographic Observations

The morphology of chromite within the komatiitic rocks at the Alexo Mine area are similar to those observed in other komatiitic units elsewhere around the world (Barnes 1998). Typically, chromite from the spinifex-textured komatiite of the A zone exhibits sub-euhedral and skeletal crystal shapes (Figure 46.4A). In contrast, chromite from the olivine cumulate of the B zones exhibits euhedral to sub-euhedral crystal shapes and are distributed as small clusters of several grains (Figure 46.4B). Euhedral chromite grains were also observed within massive sulphides at the base of the mineralized flow (sample MGH140; Figure 46.4D); however, Houlé, Leshner and Davis (2012) have also reported “hopper” to skeletal

chromite crystals along the basal contact between the komatiite unit and its footwall rocks. These observations suggest that chromite morphology is clearly dependant of the cooling environment within each komatiitic units (Barnes 1998).

In all samples investigated, almost all chromites exhibit some evidence of different degrees of alteration, which is expressed by the presence of thin rim of ferrichromite to magnetite surrounding a preserved primary chromite core (Figure 46.4C). To obtain the primary magmatic composition of the chromite, analyses were done within the core of each chromite grain (avoiding any fractures and/or inclusions).

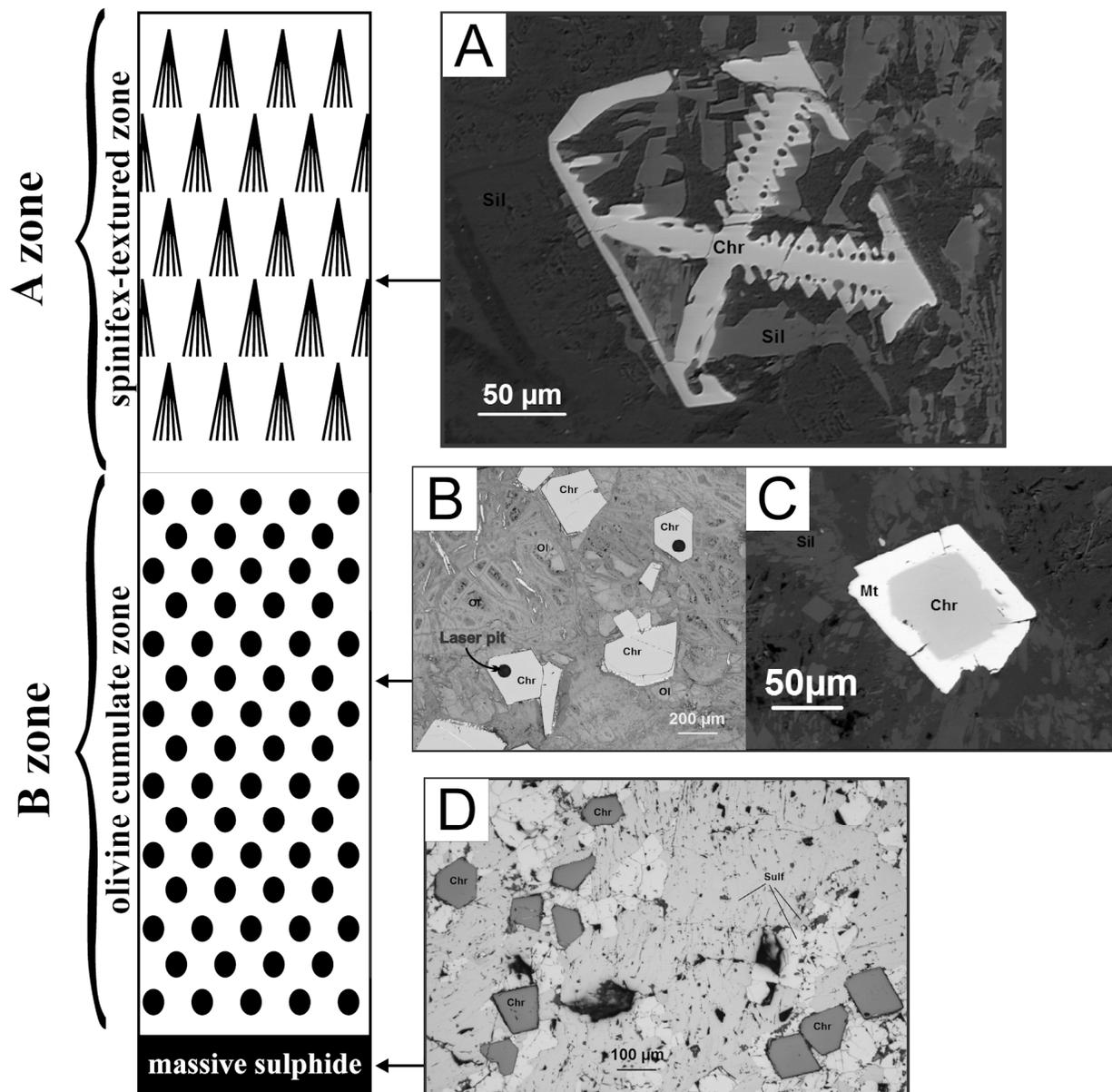


Figure 46.4. Idealized and schematic profile (not to scale) through a komatiitic unit (left) and photos of chromite with different morphologies relative to their position at the Alexo Mine area (right). A) Skeletal chromite from the spinifex-textured zone (A zone); B) euhedral chromite from an olivine cumulate (B zone); C) euhedral-altered chromite characterized by a well-preserved chromite core surrounded by a rim of magnetite within an olivine cumulate (B zone); D) euhedral chromite within a massive sulphide horizon at the base of a komatiitic flow within (Alexo member). Abbreviations: Chr = chromite; Sil = silicate; Ol = olivine; Mt = magnetite; sulf = sulphide.

Mineralogical Analysis

Chromites from mineralized and unmineralized komatiitic units were analyzed by electron microprobe and LA-ICP-MS to characterize their composition in terms of major (Cr, Al, Fe, Mg), minor and trace (Ti, Ni, Mn, V, Zn, Co, Ga, Sc), and ultra-trace (Os, Ir, Ru and Rh) elements. This section presents the preliminary results from 36 and 26 thin sections analyzed by electron microprobe and LA-ICP-MS, respectively. Between 2 to 5 chromite grains were analyzed per thin section.

ELECTRON MICROPROBE ANALYSIS

Figure 46.5 presents $Fe^{2+\#}$ ($100 \times Fe^{2+}/(Fe^{2+}+Mg)$) versus $Cr \#$ ($100 \times Cr/(Cr+Al)$) of chromite from our preliminary data for the mineralized and unmineralized komatiitic units at the Alexo Mine area in comparison with the broad field of chromite (shown in light grey) from komatiites from the compilation by Barnes and Roeder (2001). Figure 46.5 also includes a subgroup of chromite (shown in medium grey) from komatiites exhibiting low metamorphic grade (greenschist facies; Barnes and Roeder 2001). The chromite grains from our samples show $Cr \#$ ranging from 63 to 78 and $Fe^{2+\#}$ ranging from 31 to 78. As expected, the chromite from our samples compared well with the chromite from slightly metamorphosed komatiites. However, one of our samples (MGH140), containing massive sulphide, shows chromite grains with a composition clearly different from the chromite from the unmineralized komatiites. The chromites from this sample (MGH140) show high $Fe^{2+\#}$ (61 to 65) and much higher $Cr \#$ (96 to 99).

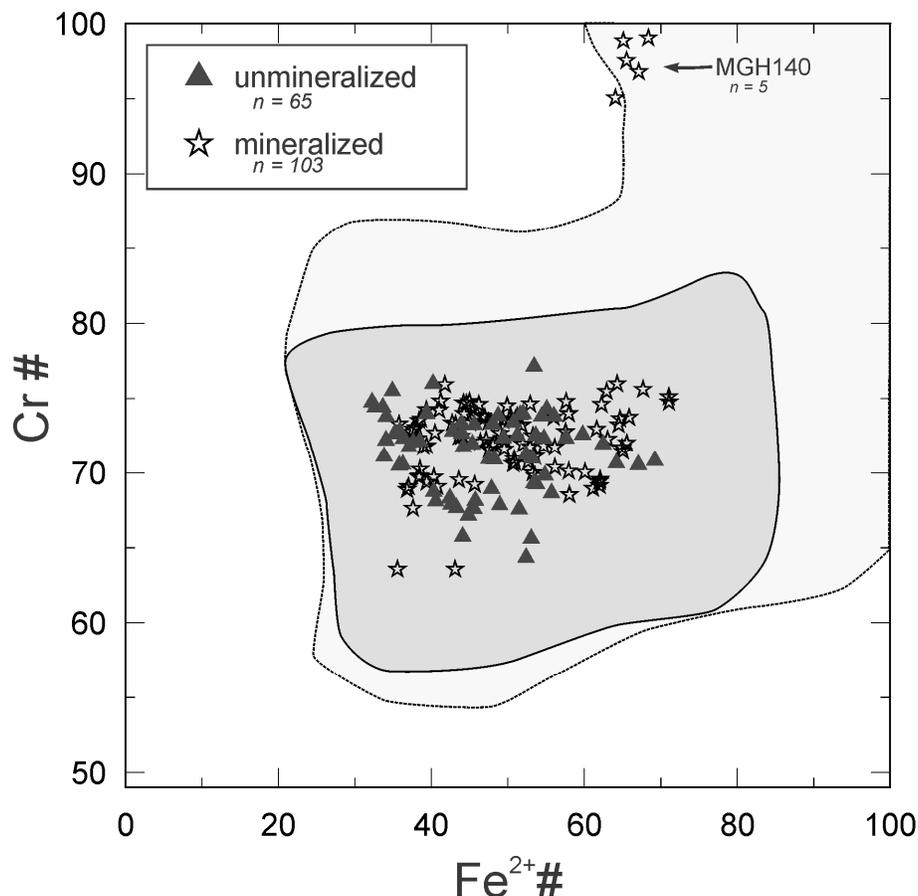


Figure 46.5. $Fe^{2+\#}$ ($= 100 \times Fe^{2+}/(Fe^{2+}+Mg)$) versus $Cr \#$ ($= 100 \times Cr/(Cr+Al)$) of chromite in komatiites from the Alexo Mine area (this study) compared with the compilation of chromite in komatiites from Barnes and Roeder (2001); light grey field = all chromites from komatiites around the world ($n=4095$); medium grey field = chromites from komatiites at greenschist facies ($n=1036$).

LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC ANALYSES

Chromite cores were analyzed using LA-ICP-MS and concentrations of 32 elements were measured, 10 of which (Mg, Al, Si, S, Ca, Cr, Cu, Sr, Pt and Pd) were used to control the nature of the ablated material and the potential presence of inclusions in the chromite. A number of elements (Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Zr, Nb, Mo, Ru, Rh, In, Os and Ir) are well above detection limits, whereas other elements (Y, Pd, Sn, Sb, Hf and Ta) were mostly below detection limits. Figure 46.6 presents binary plots for Cr # versus scandium, gallium, titanium and vanadium and for Fe²⁺# versus nickel, cobalt, manganese and zinc for mineralized and unmineralized samples. In terms of minor and trace elements, chromites from Alexo Mine komatiites show 700 to 2100 ppm V, 1400 to 3700 ppm Ti, 3 to 37 ppm Ga and 1 to 14 ppm Sc. These multivalent (³⁺ and ⁴⁺) elements show negative correlations with Cr #. For the divalent elements, chromites from Alexo Mine komatiites show 470 to 3700 ppm Zn, 1200 to 2300 ppm Mn, 150 to 350 ppm Co and 350 to 2000 ppm Ni. Zinc, manganese and cobalt show positive correlations with Fe²⁺#. Nickel shows a contrasting behaviour compared with the other divalent elements; it shows a negative correlation with Fe²⁺#. All these trends can be interpreted as being the result of fractionation. During the magmatic differentiation, Cr # decreases whereas Fe²⁺# increases. We note that with Cr # there is no discrimination between mineralized and unmineralized for almost all samples, but with Fe²⁺# some samples present a higher Fe²⁺#, a higher content in zinc, manganese and cobalt, and a lower content in nickel; however, such contents could be explained by a stronger alteration of these samples (*see* Figure 46.6; Barnes 2000). Sample MGH140 was excluded from the diagrams because of a very different content in all of these elements; indeed, this sample presents very high contents of 9300 to 12 000 ppm Ti, 5200 to 6300 ppm Mn, 1750 to 2250 ppm Zn and 2650 to 3200 ppm V; high contents of 38 to 47 ppm Ga and 10 to 16 ppm Sc; and lower contents of 160 to 260 ppm Co and 320 to 410 Ni. Sample Ax33 is excluded from fractionation trends (*see* Figure 46.6) because of differences in content for all elements presented. In Cr # diagrams, sample Ax33 presents a high content relative to other samples of 1600 to 2000 ppm V and a low content of 1500 to 1700 ppm Ti, 3 to 25 ppm Ga and 1 to 6 ppm Sc. In Fe²⁺# diagrams, sample Ax33 presents a high Fe²⁺# (~76); a higher content of 15 000 to 26 000 ppm Zn, 4300 to 5900 ppm Mn and 350 to 400 ppm Co; and a lower content of 95 to 175 ppm Ni. Sample Ax33 is the only sample where chromites a) show evidence of alteration by the presence of a large magnetite rim and by distinctive geochemical signatures that could reflect the effect of alteration, and b) show lower scandium, gallium and nickel contents and enrichment in iron, zinc, manganese and cobalt; all these characteristics are indicators of metamorphosed chromites (Barnes 2000).

As was mentioned previously, platinum group elements are extremely sensitive, especially ruthenium, to the presence of an immiscible sulphide liquid that has the capacity to scavenge most of the PGE available in the komatiitic magma, thus affecting the composition of chromite formed subsequently (e.g., Righter et al. 2004). The results obtained so far indicate analytical signals above detection limits for osmium, iridium, rhenium and ruthenium for most of the chromite from the mineralized and unmineralized samples. Ruthenium is detected above detection limit from most of the 26 samples for which chromites have been analyzed, but 3 of the samples have ruthenium concentrations close to or below the detection limit (60 ppb): these samples include 2 samples from the mineralized flows, Ax33 (n=4) and the massive sulphide MGH140 (n=5), and 1 sample from the unmineralized flow, Ax69 (n=3) (Figure 46.7). The chromites from Alexo Mine contain low concentrations (close to the detection limit) of osmium, iridium and rhenium varying from 7 ppb (detection limit) to 30 ppb. On the other hand, most of the chromites from Alexo Mine contain significantly higher concentrations of ruthenium varying from 6 ppb (below detection limit) up to 430 ppb (*see* Figure 46.7). As shown on Figure 46.7, we note ruthenium shows a weak positive correlation with Cr #, a trend that could also be related to fractionation.

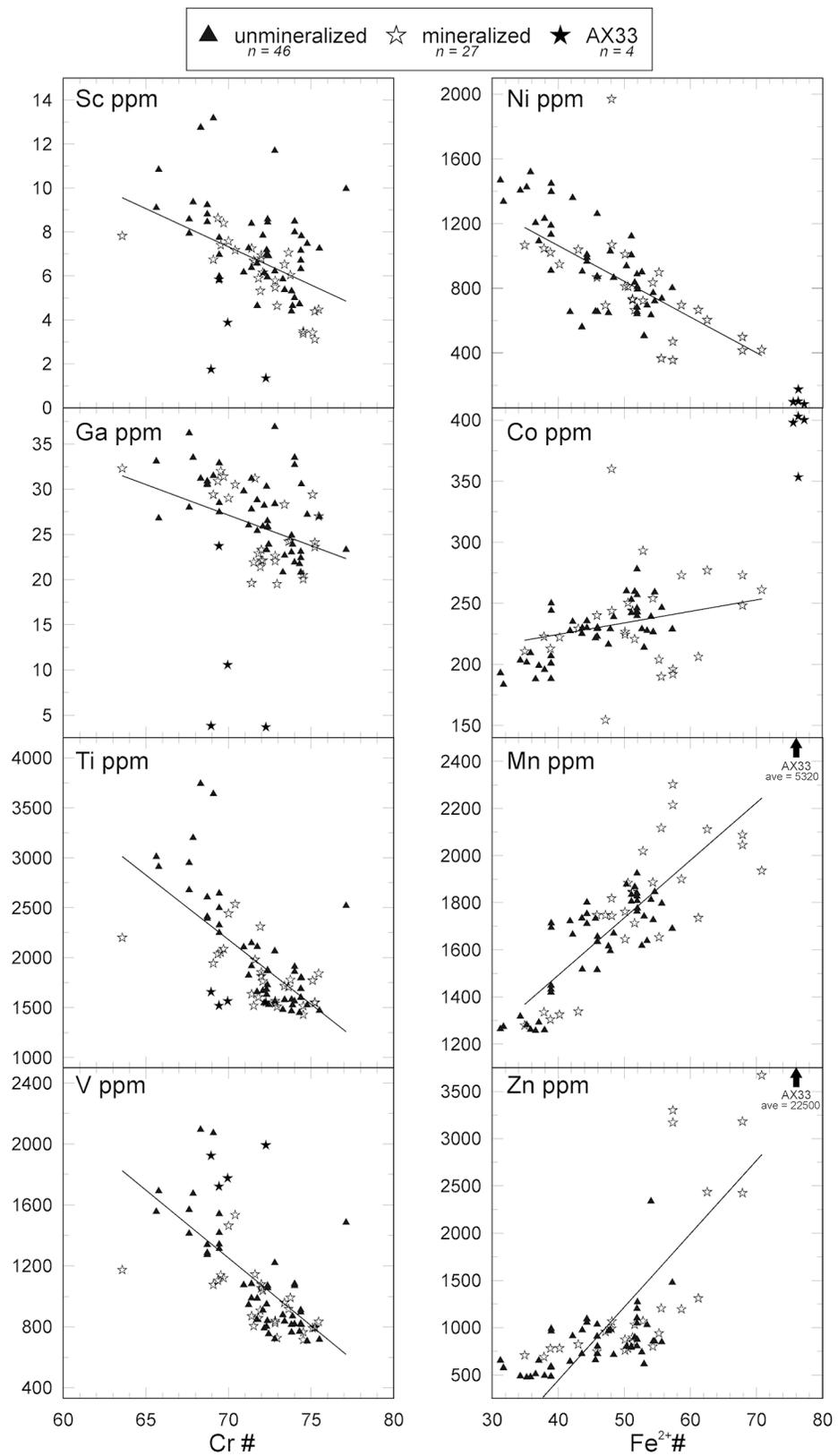


Figure 46.6. Binary plots showing, on the left, Cr # versus scandium, gallium, titanium and vanadium content, respectively; and, on the right, Fe²⁺ # versus nickel, cobalt, manganese and zinc content, respectively. Solid lines = linear regression lines.

SUMMARY

Preliminary results of the chromite geochemistry shows that vanadium, titanium, gallium, scandium, zinc, manganese and cobalt contents of the chromite from Alexo Mine komatiites increase with magmatic differentiation, represented by the decrease of Cr # and the increase of Fe²⁺ #. However, nickel shows an inverse correlation with Fe²⁺ #, and correlates very well with the magnesium content of chromites. Overall, these relations seem to reflect the effect of fractionation of komatiitic magmas. Ruthenium concentration ranges below detection level up to 430 ppb, and the positive correlation could also be related to the effect of fractionation of komatiitic magmas. It is noted that, based on analyses to date, trace elements and ruthenium do not discriminate mineralized and unmineralized units at the Alexo Mine area. However, it is interesting to note that at least some of the chromite formed with sulphide droplets exhibits depletion in ruthenium that results from a much higher partition coefficient for sulphide than for chromite (e.g., sample MGH140). One of the main goals of this study is to evaluate if the PGE content of chromite can be used as an exploration tool for mineralized komatiitic systems. In the light of these new results, the high concentration in ruthenium in chromites from some of the mineralized samples could be explained either by i) the fact that Alexo Mine komatiites are probably an open system as proposed by Houlé, Leshner and Davis (2012) (i.e., flow-through systems) and ruthenium depletion signature of the chromite within these mineralized units have been flushed out of this system or ii) the fact that chromite could have crystallized before the sulphide segregation, or concomitantly with sulphide segregation (i.e., pre- to syn-sulphide). However, further investigation is needed to confirm these hypothesis.

FUTURE WORK

These preliminary results still need to be analyzed and evaluated further to better understand the behaviour of the PGE, especially ruthenium, in the presence or absence of an immiscible sulphide liquid. Additional chromite electron microprobe and LA-ICP-MS analyses will be carried out on mineralized and barren komatiitic units from the Alexo Mine area, after which we will be able to observe if there is a

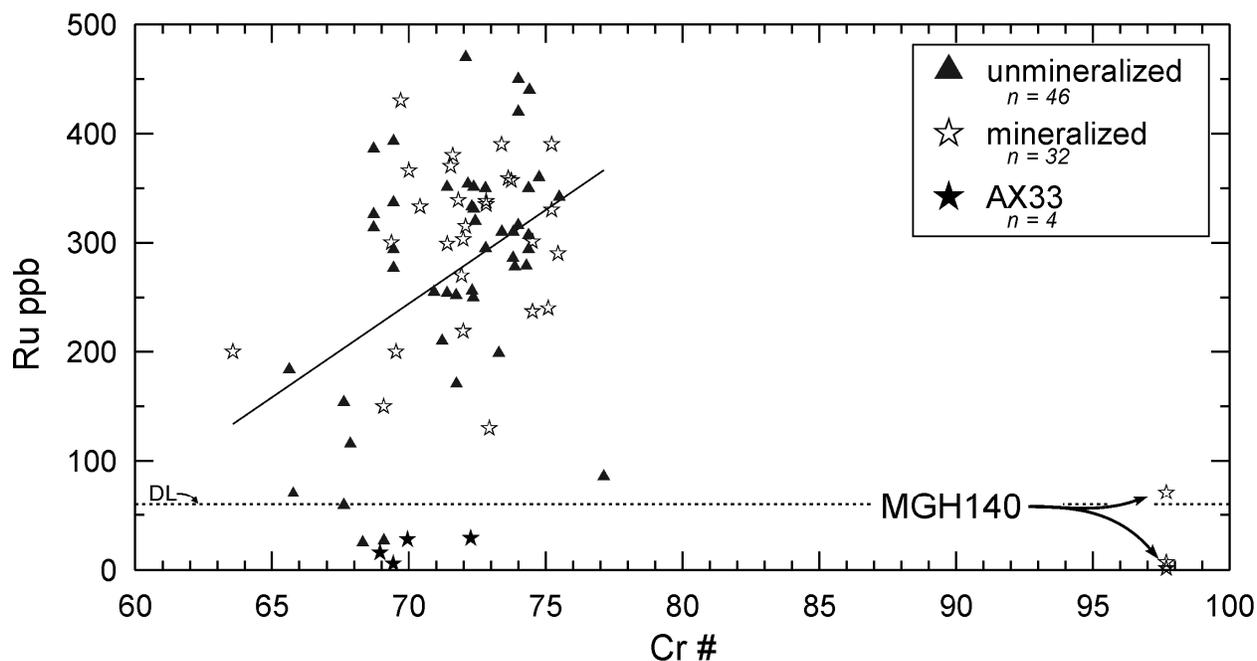


Figure 46.7. Diagram showing the concentrations of Cr # versus ruthenium (ppb) for chromites from the Alexo komatiites. Solid line = linear regression line; DL = detection limit.

variation in chromite geochemistry relative to the position relative to the mineralization (from distal to proximal). In addition, whole rock analyses will be used to perform mass balance calculations to determine which elements are controlled and influenced by the chromite and sulphide crystallization.

ACKNOWLEDGMENTS

This study is part of a MSc project based at Université du Québec à Chicoutimi (UQAC, Saguenay) under the supervision of Drs. P. Pagé (UQAC), S.-J. Barnes (UQAC), and M.G. Houlé (GSC-Québec). The project has been funded by the Geological Survey of Canada under the Targeted Geoscience Initiative 4 (TGI-4) and the Canada Research Chair of Magmatic Ore Deposits. We also thank Anne-Aurélié Sappin (GSC) for her review of the manuscript that helped us improve the final version of this report. This is Geological Survey of Canada contribution number 20120251.

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