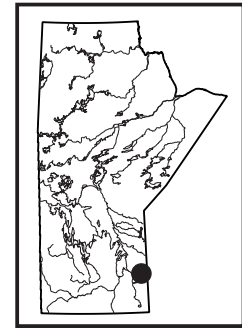


**Mineral chemistry of chromite in the Mayville intrusion:
evidence for petrogenesis and linkage to the Bird River sill in the
Neoproterozoic Bird River greenstone belt, southeastern Manitoba
(parts of NTS 52L5, 6, 12)**

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Summary

In 2014, the Manitoba Geological Survey completed bedrock mapping in the northern arm of the Bird River greenstone belt of the western Superior province, southeastern Manitoba. The project aim was to provide fundamental geoscientific information to assist mineral exploration, in particular for magmatic Ni–Cu–platinum group element (PGE)–Cr mineralization associated with mafic–ultramafic intrusions in the region. Because mafic–ultramafic rocks are readily altered by deformation, metamorphism, magmatism and related hydrothermal systems, their primary mineral assemblages and geochemical composition are typically modified, requiring more robust geochemical techniques to ‘see through’ these effects. Consequently, the mineral chemistry of chromite, which is highly refractory and resistant to chemical modification, has been examined to help evaluate the affinity and fertility of mafic–ultramafic systems in the Bird River belt.

This report presents chemical composition data on chromite from the Neoproterozoic Mayville mafic–ultramafic intrusion (MI) in the north arm of the Bird River greenstone belt, and compares them to that of chromite in the Bird River sill (BRS) in the southern limb of the belt, in order to provide insight into the magmatic affinity, magmatic processes, tectonic setting and petrogenetic relationships. Chromite in the MI is characterized by higher Fe-number ($Fe\# = 100 \times Fe^{2+} / [Fe^{2+} + Mg^{2+}]$) and Al/Mg ratio, variable Cr-number ($Cr\# = 100 \times Cr^{3+} / [Cr^{3+} + Al^{3+}]$) and lower Mg-number ($Mg\# = 100 \times Mg^{2+} / [Mg^{2+} + Fe^{2+}]$) compared to that in the BRS. This indicates that the parent magma(s) to the MI is/are of tholeiitic affinity, like those of the BRS but more evolved, and may have been derived from subcontinental aluminous lithospheric mantle enriched by slab melt(s) related to plate subduction. In contrast, the parental magma(s) to the BRS was/were less evolved and may have been sourced from more depleted subcontinental lithosphere mantle. Although the MI is synchronous with the BRS and both are thus related to the extensive ‘Bird River magmatic event’ proposed by Houlié et al. (2013), they are interpreted to result from different petrogenetic processes that reflect either different sources or degrees of differentiation. This study complements detailed bedrock mapping and litho-geochemical investigations, and indicates that the MI is fertile for

Ni–Cu–PGE mineralization, in accord with the widespread occurrence of contact-style magmatic sulphide mineralization near the base of the heterolithic breccia zone (HBZ) and at the basal contact of the intrusion. Furthermore, the MI is prospective for reef-style, stratiform PGE mineralization in transitional and/or contact zones between major rock units, and for stratiform chromitite mineralization as demonstrated by the presence of massive chromitite bands and disrupted chromitite–pyroxenite layers within the HBZ.

Introduction

In 2014, the Manitoba Geological Survey (MGS) continued the multiyear mapping project in the northern arm of the Bird River greenstone belt (BRGB) of the western Superior province in southeastern Manitoba (Figure GS-3-1). This project has been conducted by the MGS in collaboration with the Geological Survey of Canada (GSC) through a Targeted Geoscience Initiative 4 program, which was supported by Mustang Minerals Corp. (MMC). The main objectives of the project are to

- update the regional bedrock map in the Cat Creek and Cat Lake–Euclid Lake areas;
- address the geological evolution and geodynamic environment of the BRGB; and
- assess the metallogeny of magmatic Ni–Cu–PGE sulphide and Cr mineralization associated with mafic–ultramafic intrusions within the BRGB.

The northern arm of the BRGB, including the Mayville mafic–ultramafic intrusion (MI) and surrounding rocks in the Cat Creek area, were mapped by the MGS in 2012 at 1:12 500 scale. This bedrock geology map has been revised, expanded and upgraded to 1:10 000 scale (Yang, 2014) based on data acquired in the last two years (Figure GS-3-2). The MI is a composite layered intrusion, comprising dominantly gabbroic–anorthositic rocks with minor ultramafic components, which was intruded into mid-ocean-ridge basalt (MORB)–type basalts overlying Mesoproterozoic basement represented by the Maskwa Lake batholith I (Yang et al., 2012, 2013). Bedrock mapping and exploration drilling indicate that Ni–Cu–PGE–Cr mineralization is hosted mostly in the mafic–ultramafic units in the lower part, and/or at the base, of the MI. Since the MI underwent regional metamorphism and was intruded

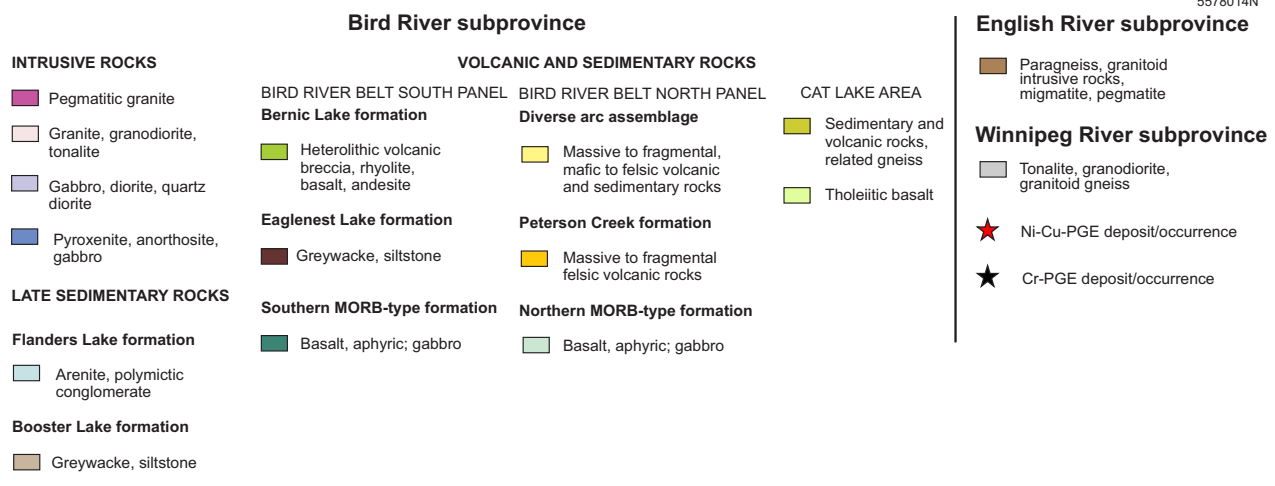
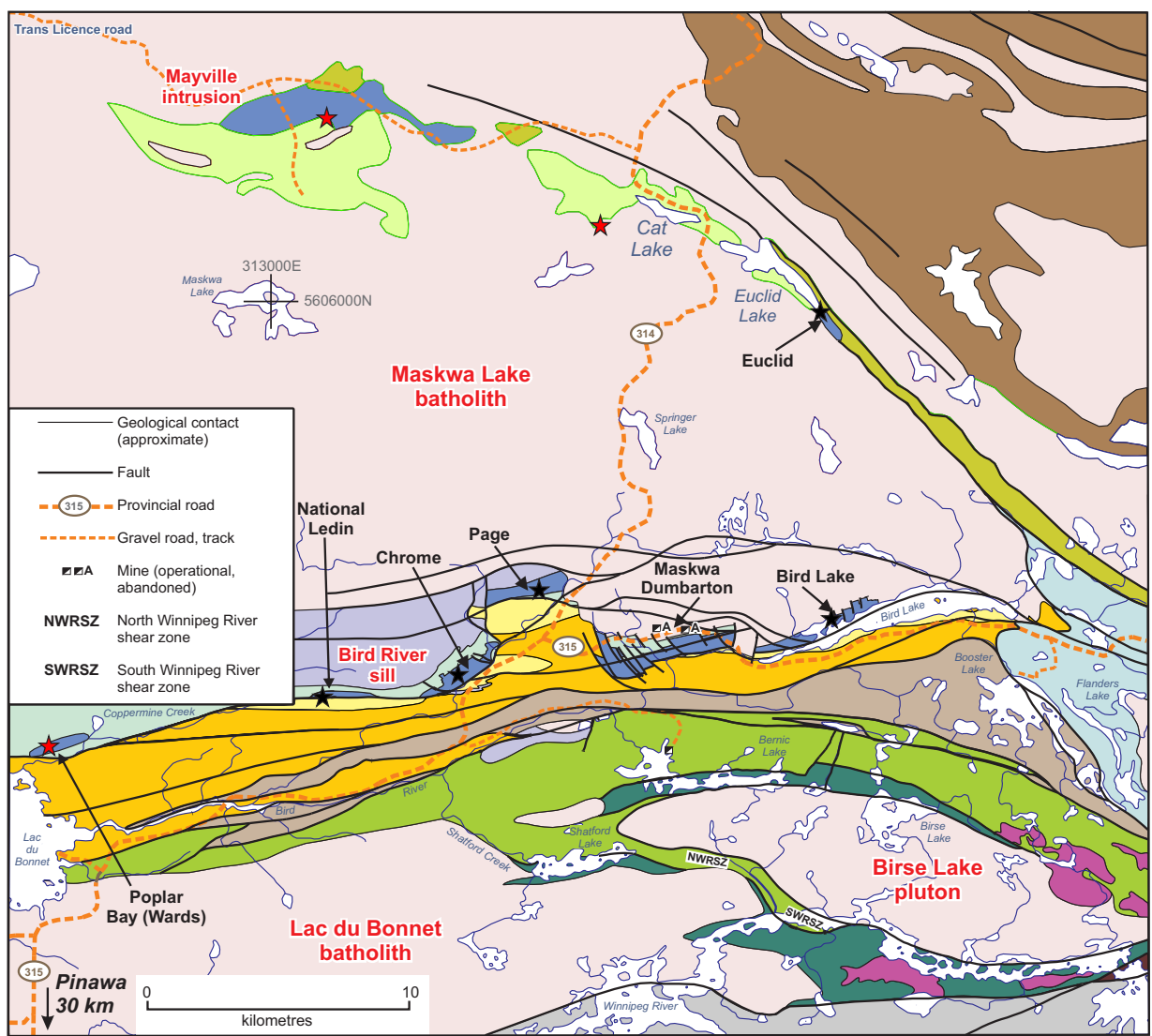


Figure GS-3-1: Regional geology between Cat Lake–Euclid Lake and the Winnipeg River, southeastern Manitoba, showing the southern arm of the Bird River greenstone belt between Lac du Bonnet and Flanders Lake, and the northern arm extending as far as the Mayville intrusion. Locations of chromite deposits (e.g., Chrome property, Euclid Lake) marked by black stars.

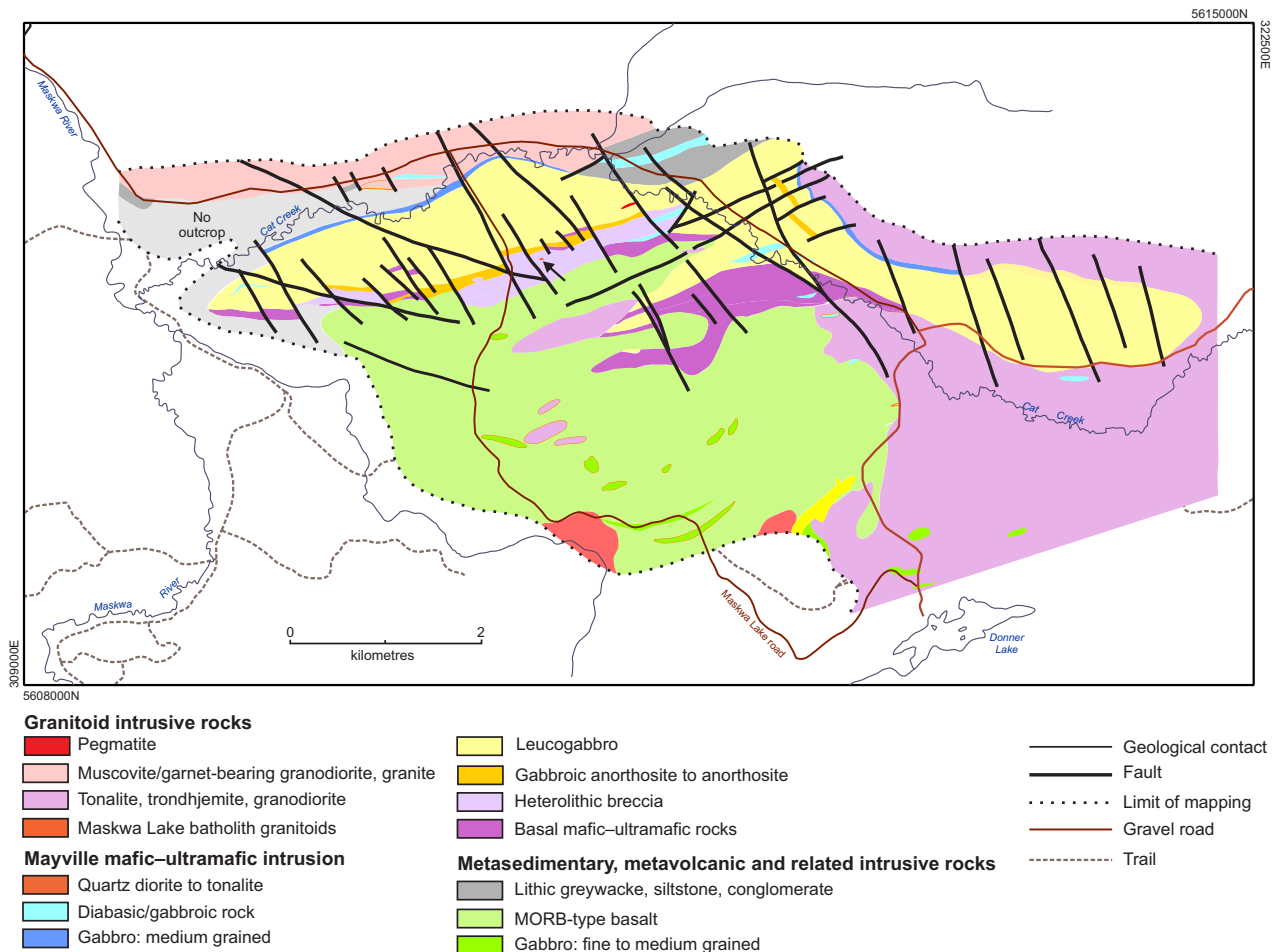


Figure GS-3-2: Simplified geological map of the Neoproterozoic Mayville intrusion in the northern arm of the Bird River greenstone belt, southeastern Manitoba (modified after Yang, 2014). A quartz diorite to tonalite (unit 10) dike (or dikes) within the Mayville intrusion is/are indicated by the orange dot (not to scale) at the end of the black arrow.

by Neoproterozoic tonalite, trondhjemite and granodiorite (TTG; e.g., Peck et al., 2002; Yang and Gilbert, 2014), its primary mineral assemblages and lithogeochemical characteristics were strongly modified, although magmatic textures are generally well preserved (Peck et al., 1999; Yang et al., 2011, 2012). Due to its highly refractory nature, chromite in the MI provides a record of the primary geochemical signatures of the magmas, which are essential in evaluating its fertility for Ni-Cu-PGE-Cr mineralization and for exploration targeting.

This report concentrates on the Neoproterozoic MI (2742.8 ± 0.8 Ma; see Houlié et al., 2013) by using chromite chemistry as a tool to investigate its magmatic affinity, magmatic processes and tectonic setting(s), and to compare them with those of the Bird River sill (BRS) in the southern limb of the BRGB in order to investigate the possibility of a petrogenetic relationship.

A brief background on chromite studies is provided before the results of work on the Mayville chromite are

presented, to show the important role played by this mineral in investigations of petrogenesis of mafic-ultramafic rocks and in mineral exploration.

Brief review of chromite studies

Chromite ($\text{Fe}^{2+}\text{Cr}_2\text{O}_4$) is an end member of the spinel group of minerals, whose formula is AB_2O_4 (where A is Fe^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} or Zn^{2+} in four-fold co-ordination *T* sites and B is Cr^{3+} , Fe^{3+} , Al^{3+} or Ti^{4+} in six-fold co-ordination *M* sites; Deer et al., 1962, 1992). Spinel group minerals have long been used as ‘petrogenetic indicators’ (Irvine, 1965, 1967), because 1) they crystallize over a wide range of conditions from mafic-ultramafic magmas; 2) are among the first phase(s) to crystallize; 3) display a wide range of solid solution; and 4) are relatively refractory and resistant to alteration and metamorphism compared to other high-temperature magmatic silicate minerals, such as olivine or orthopyroxene (Peck and Keays, 1990; Barnes, 1998, 2000; Barnes and Roeder,

2001; Sobolev and Logvinova, 2005; Rollinson et al., 2010; Krause et al., 2011; Voigt and von der Handt, 2011).

The cores of chromite crystals may retain their original magmatic chemistry at metamorphic temperatures of up to 500°C (Barnes, 1998) or even higher (Rollinson et al., 2010). Therefore, chromite chemistry has proven to be an effective tool to investigate magma types, magmatic processes and tectonic settings in metamorphosed mafic–ultramafic intrusions (Irvine, 1965; Roeder, 1994; Stowe, 1994; Barnes, 1998, 2000; Barnes and Roeder, 2001; Kamenetsky et al., 2001; Arif and Jan, 2006). Chemical composition of spinel minerals can also be used to identify Ni-mineralized and -barren mafic–ultramafic intrusions (Yang et al., 1994; Barnes and Tang, 1999; Barnes and Kunilov, 2000). Therefore, spinel is one of the best index minerals for Ni-Cu-PGE-Cr exploration. Moreover, chromite included in diamonds displays a relatively narrow Cr# range ($100 \times \text{Cr}^{3+}/[\text{Cr}^{3+} + \text{Al}^{3+}] = 75\text{--}90$) but variable Mg# ($100 \times \text{Mg}^{2+}/[\text{Mg}^{2+} + \text{Fe}^{2+}] = 50\text{--}80$), thus making it an ideal indicator for diamond exploration (Sobolev and Logvinova, 2005).

Previous work

Chromite and chromitite seams occur in various mafic–ultramafic intrusions, including the MI and BRS in the northern and southern arms of the BRGB, respectively (Figure GS-3-1; Stevenson et al., 2001; Bailes et al., 2003; Lemkow et al., 2006; Gilbert et al., 2008). Multiple generations of deformation, metamorphism and magmatism have influenced the entire belt (Trueman, 1980; Duguet et al., 2009).

Mayville intrusion

The MI is a layered composite intrusion consisting predominantly of gabbroic–anorthositic rocks with minor ultramafic components (Figure GS-3-2; Yang, 2014). Chromite is present mostly in the heterolithic breccia zone (HBZ; Peck et al., 1999; Yang et al., 2012) as 1) chromitite bands or layers; 2) disseminations in pyroxenite and gabbro; and 3) discrete crystals in the reaction zones between leucogabbro (blocks) and ultramafic rocks in the MI, as described by Hiebert (2003). Chromitite layers up to 0.4 m thick, consisting of ~30–50 mode % chromite, plus amphibole, chlorite and minor sulphide, occur within the upper HBZ (Figure GS-3-3a, b). Some chromite grains contain exsolution lamellae of ilmenite and/or rutile (Figure GS-3-3c), confirming the observations of Hiebert (2003). This style of chromitite is similar to the BRS, where the Chromitiferous zone, comprising chromitite bands or layers, is also present at the top of the Ultramafic series (Scoates et al., 1986, 1989; Williamson, 1990). Some chromitite layers in pyroxenite are strongly magnetic, whereas others are lens-like rafts that are not magnetic (Figure GS-3-3d, e). Disseminated chromite usually occurs in ultramafic dikes in the heterolithic

unit, which contains scattered disseminated pyrrhotite and chalcopyrite (Figure GS-3-3f). It is noted that some chromite crystals contain rounded inclusions of silicate melt (Figure GS-3-3g), suggesting that chromite crystallized from a silicate melt. Compositional zoning is not uncommon in Mayville chromite (Figure GS-3-3h), indicating that it was likely buffered by the melt composition. Pyrrhotite inclusions are evident in chromite, suggesting that sulphide saturation may have occurred earlier (Hiebert, 2003; Yang et al., 2011, 2012), perhaps resulting in Ni, Cu and PGE depletion in the evolved residual magma(s).

Hiebert (2003) investigated the chemical composition of chromite from the MI, concluding that it is generally characterized by much lower MgO/(MgO+FeO) ratios than those in the BRS (as determined by Gait, 1964). This suggests that the magmas from which the MI crystallized may have been relatively more evolved, consistent with petrological and lithochemical features (Theyer, 1991, 2003; Peck et al., 1999, 2000; Yang et al., 2011, 2012). It is noted that Hiebert (2003) only analyzed five elements (i.e., Al₂O₃, MgO, Cr₂O₃, TiO₂, FeO). Full characterization of the chemistry of chromite, however, also requires analysis of NiO, CoO, MnO and ZnO (see Barnes and Roeder, 2001; Rollinson et al., 2010).

In this study, 17 samples from the MI were collected for petrographic investigation and chemical analysis of chromite to characterize the chemical signatures and magmatic affinity, and compare them with those of chromite in the Bird River sill. The nature of the parent magma from which the MI formed is also assessed using chromite chemistry. As mentioned in the above brief review of chromite studies, the cores of refractory chromite grains may record information regarding the magma from which it crystallized, whereas rim composition of the chromite may reflect re-equilibrium with interstitial residual melt (silicate liquid).

Bird River sill

In the BRS, six groups of chromitite layers occur in the Chromitiferous zone, which is about 60 m thick and consists of alternating layers of peridotite and chromitite (Figure GS-3-4; Scoates et al., 1986, 1989; Williamson, 1990). The chromitite layers or bands are well exposed at the Chrome property (Figure GS-3-1), where the entire stratigraphy of the BRS is also exposed. Three representative samples were collected from the Upper Main section of the Chromitiferous zone for chemical analysis of chromite in this study, and previous chromite data from Gait (1964) were also compiled to characterize the chemical composition of chromite in the BRS. Type chromitite from the BRS is shown in Figure GS-3-5.

The chemistry of chromite in the BRS was studied by Bateman (1945) after this mineral had been identified (Brownell, 1942; Bateman, 1943), suggesting an excess of Fe₂O₃ present as exsolved hematite in some chromite

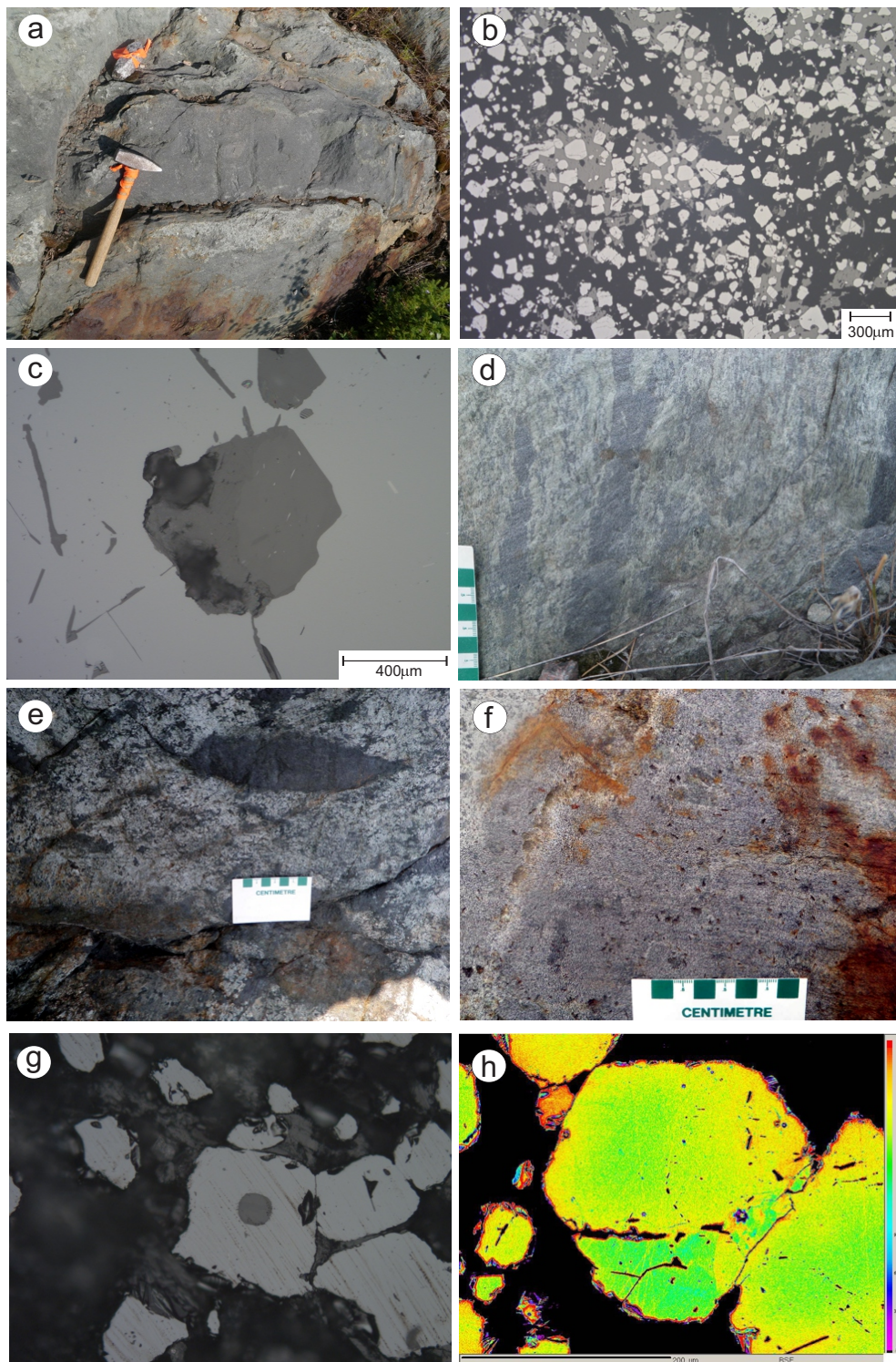


Figure GS-3-3: Field photographs of chromite occurrences and representative photomicrographs of chromite crystals in the Mayville intrusion, Cat Creek area, southeastern Manitoba: **a)** disrupted, ~40 cm thick, nonmagnetic chromitite band in pyroxenite (UTM Zone 15N, 314616E, 5612596N, NAD83) from the heterolithic breccia unit; **b)** euhedral to subhedral chromite crystals (scale bar is 100 μm) in the massive chromitite band (sample 111-12-500B1; location same as (a); reflected polarized light [RPL]); **c)** exsolved lamellae in a chromite crystal (sample 111-12-500B1; RPL); **d)** strongly magnetic chromitite layers in pyroxenite (UTM 314606E, 5612599N); **e)** lens-like chromitite raft in pyroxenite (UTM 314606E, 5612599N); **f)** disseminated chromite in an ultramafic dike from the heterolithic unit that also contains scattered disseminated pyrrhotite and chalcopyrite (UTM 314616E, 5612473N); **g)** spherical inclusion of silicate melt, about 25 μm in size, in a subhedral chromite crystal with resorbed edges (sample 111-12-500B1; RPL); **h)** back-scattered electron image with pseudocolour, showing compositional zonation or heterogeneities in chromite (sample 111-12-500B1).

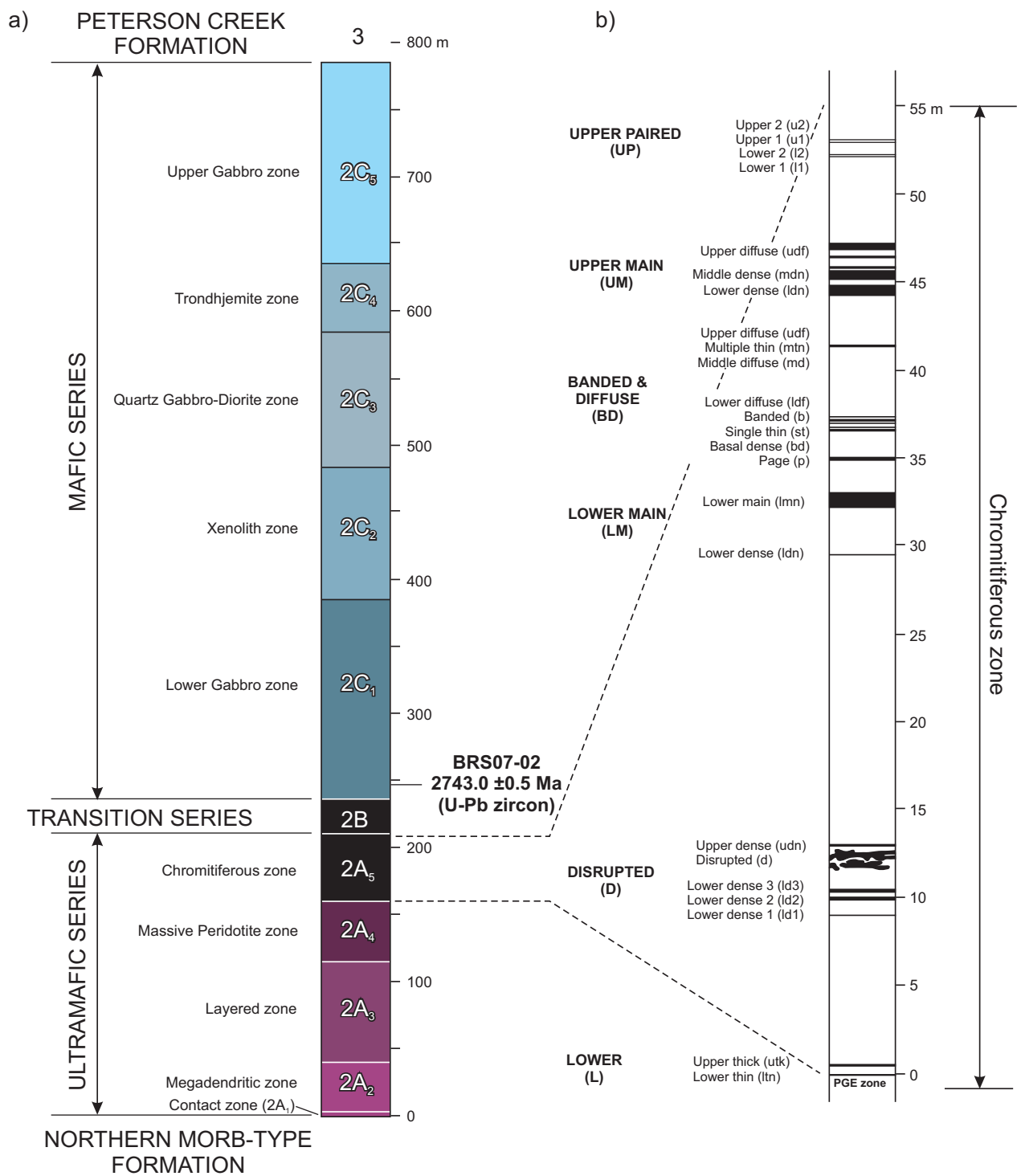


Figure GS-3-4: Stratigraphic column of the Bird River sill (a) and subdivision of its Chromitiferous zone into six groups (b) at the Chrome property in the southern arm of Bird River greenstone belt, southeastern Manitoba: Lower, Disrupted, Lower Main, Banded and Diffuse, Upper Main and Upper Paired sections (after Williamson, 1990). Also shown is the approximate stratigraphic position of the U-Pb age determination (2743.0 ± 0.5 Ma) by Scoates and Scoates (2013), who interpreted it as the crystallization age of the Bird River sill.

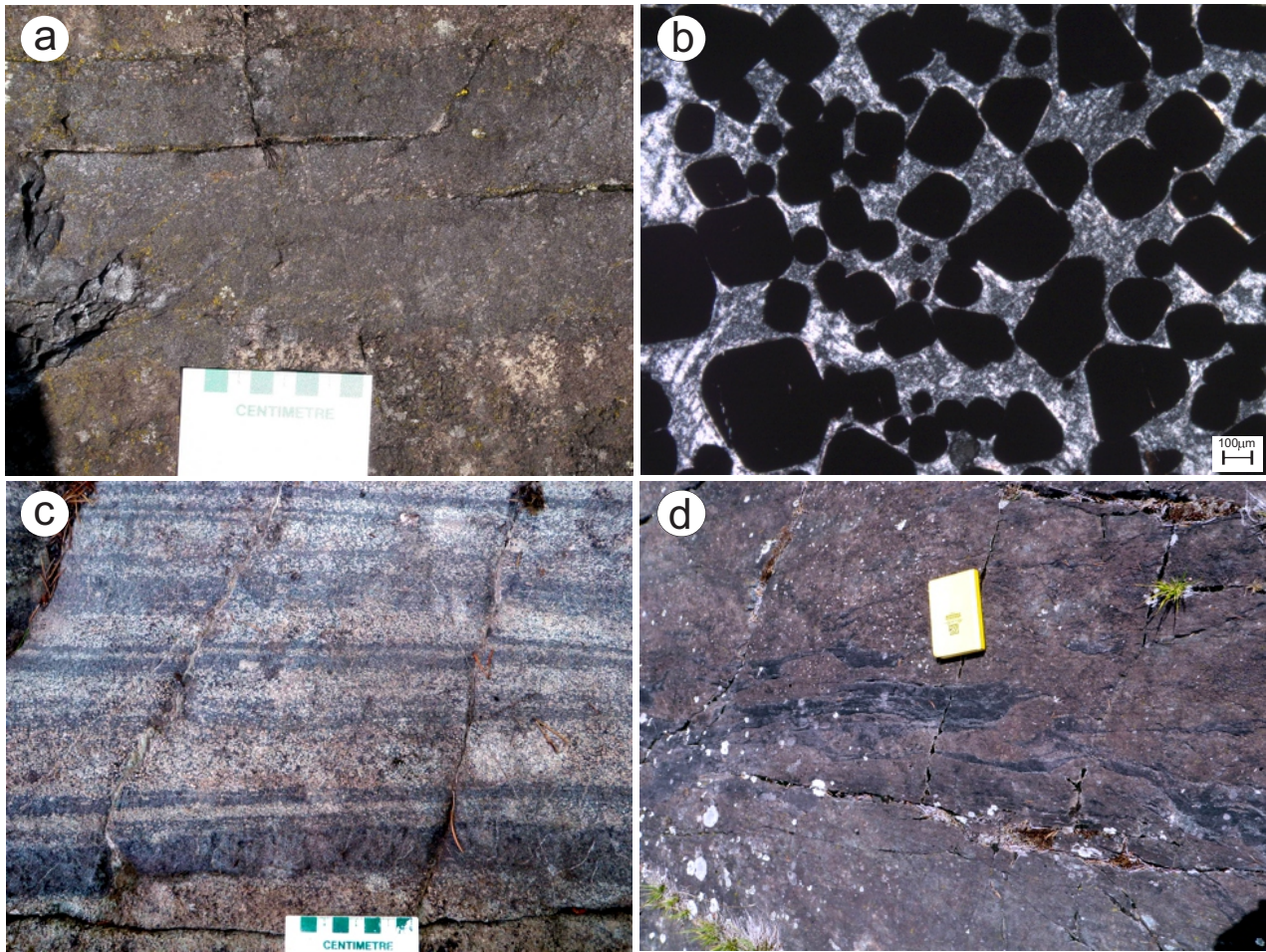


Figure GS-3-5: Field photographs of chromite occurrences and representative photomicrograph of chromite crystals from the Chrome property, Bird River sill, southeastern Manitoba: **a)** massive, ~20 cm thick, nonmagnetic chromitite band in peridotite (UTM Zone 15N, 318414E, 5592677N, NAD83); **b)** euhedral to subhedral chromite crystals (scale bar is 100 μm) in the massive chromitite band (sample 111-11-18; location is the same as (a)); transmitted plane-polarized light; **c)** multiple thin chromitite layers in peridotite (UTM 318425E, 5592685N); **d)** disrupted chromitite subunit hosted by peridotite (UTM 318270E, 5592688N).

specimens. This finding was confirmed by Gait (1964) through a heating experiment in which a hematite rim and/or laminae exsolved from chromite on heating at 1000°C in a furnace without controlling oxygen fugacity.

Scoates et al. (1986, 1989) presented a plot of Cr# versus Mg# to portray the chemical compositions of chromite from the six chromitite layer groups in the BRS, and suggested that an earlier magmatic trend controlled by fractionation of the ultramafic–mafic magmas led to increasing Cr# (from ~50 to 70) with decreasing Mg# (from 62 to 15). These authors also suggested that a late metamorphism may have elevated the Cr# (from 70 to 100) within a narrow range of Mg# (20 to 5). They attributed the magmatic trend to reaction of cumulus chromite with intercumulus liquid (silicate melt) or silicate minerals during subsolidus cooling, and the metamorphic trend to the growth of ferrichromite as rims around cores of magmatic chromite during regional metamorphism. Scoates et al. (1989) pointed out that the ratio of chromite

to silicate is a key factor controlling the interaction between chromite and silicate during metamorphism. For example, chromite from chromite-silicate cumulate with a ratio of about 1:1 was little affected by metamorphism and retains the signature of a magmatic trend, whereas chromite in olivine-chromite cumulate shows significant Fe enrichment because of the lower chromite-silicate ratio, resulting in a metamorphic trend.

Ohnenstetter et al. (1986) determined the chemical composition of chromite in the Upper Main chromitite layers defined by Scoates (1983), finding trends similar to those identified by Scoates et al. (1986, 1989). Generally, chemical composition of chromite from the BRS is consistent with those of stratiform chromite deposits associated with mafic–ultramafic intrusions, as summarized in Duke (1983).

A major PGE concentration zone (reef), ~1 m thick, is present at the base of the Chromitiferous zone (Figure

GS-3-4), which occurs at the top of the Ultramafic series. This PGE zone is associated with Lower group chromite (Figure GS-3-4) and with a subjacent interval of peridotite containing sparse, irregularly disseminated sulphide minerals (Scoates et al., 1989; Peck et al., 2002). It extends laterally about 800 m along the zone, and seems to be stratiform.

Tiny laurite (RuS_2) inclusions, 1.5–12 μm in size, together with rutheniridosmine (Os, Ir, Ru alloy), in chromite from the Chromitiferous zone are associated with pyrrhotite, chalcopyrite and pyrite (Talkington et al., 1983; Ohnenstetter et al., 1986). This suggests earlier sulphide saturation in the BRS. Ruthenium (and Ir, Os) appears to have higher capacity to combine with S^{2-} than either Ni or Fe in ultramafic melt because sulphide inclusions are dominated by laurite.

Present study

Petrography

Massive fine-grained chromite consists of 35–50 modal % euhedral to anhedral chromite, 0.02–0.3 mm in diameter, embedded in a groundmass of serpentine and chlorite (Figure GS-3-3b, -5b). Most chromite grains are unaltered, but some display minor chloritic alteration. Some chromite crystals contain rounded silicate inclusions and others have sulphide inclusions, indicating that chromite crystallized from sulphide-saturated silicate magma(s). Compositional zonation is common, mostly with an FeO^{I} -enriched rim and Cr_2O_3 -rich core (Figure GS-3-3h). However, reverse zoning is also evident. Opaque minerals are dominantly chromite, and minor ilmenite and rutile.

Disseminated chromite also occurs in pyroxenite and gabbroic rocks from the MI. The ultramafic rock is commonly coarse grained, showing adcumulus texture, and consists dominantly of hornblende (as a result of alteration of pyroxene, mostly clinopyroxene). Hornblende crystals are euhedral to subhedral, and constitute more than 90% of the mode. Some hornblende grains are strongly altered to chlorite and carbonate, and magnetite. Recrystallization of some grains is manifested by smaller amphibole aggregates. Disseminated chromite occurs as inclusions in hornblende grains, and pyrite and pyrrhotite are interstitial.

Mineral chemistry

Analytical method

The chemical composition of chromite was analyzed by electron probe microanalyzer (EPMA). The analytical work was conducted in wavelength-dispersion mode on a Cameca SX-100 electron microprobe at the University of Manitoba. Operating conditions were 15 kV accelerating voltage, 20 nA beam current and a 20-second counting

interval for both peak and total background. The beam size was set at 10 μm , except for very small chromite grains that were analyzed by using a focused beam (<1 μm). A combination of various minerals and metal standards were used to analyze for SiO_2 (0.06), TiO_2 (0.04), V_2O_5 (0.05), Al_2O_3 (0.02), Cr_2O_3 (0.05), FeO (0.06), MnO (0.03), MgO (0.03), CoO (0.06), NiO (0.07) and ZnO (0.10); the number in brackets after each oxide indicates analytical uncertainty in percent for that element. Raw data were calibrated with PAP matrix corrections. In each sample, several chromite grains were analyzed based on textural relation and analyzed positions in a crystal (e.g., rim, middle, core). An average of these analytical results was taken to represent the typical composition of the chromite in each sample, together with standard deviation. Formula calculations of chromite are based on four atoms of oxygen, and their ferric/ferrous ratios are calculated by stoichiometry and charge balance using the method of Barnes and Roeder (2001). Table GS-3-1 presents the chemical composition and structural formulas of chromite in representative samples collected from the MI and the BRS.

Chromite chemistry

Nomenclature of spinel group minerals used in this study strictly follows the recommendations of International Mineralogical Association (Nickel, 1992). Spinel minerals are named based on the most abundant trivalent cations: chromite (dominated by Cr^{3+}), spinel (Al^{3+}) or magnetite (Fe^{3+}). Accordingly, spinel minerals in the MI and the BRS are chromite that is dominated by Cr^{3+} (Table GS-3-1). Chromite in the MI has a maximum $\text{Cr}/\text{Fe}^{\text{I}}$ ratio of 1.1, whereas those in the BRS vary up to 1.8. These ratios are well within the range of stratiform chromite deposits associated with layered mafic–ultramafic intrusions but much lower than those of podiform chromite deposits related to ophiolite suites (Stowe, 1994).

It is worth noting that chromite in the BRS displays a range of $\text{Mg}\#$ from 19 to 50, but maintains a narrow, relatively high range of $\text{Cr}\#$ (52 to 76). In contrast, chromite in the MI has a range of $\text{Cr}\#$ from 31 to 83, with only a small variation in $\text{Mg}\#$ (10 to 23; see below).

Chemical composition of chromite in the MI and the BRS is well portrayed in a set of compositional diagrams suggested by Barnes and Roeder (2001), based on two common projections of the spinel prism of Stevens (1944). The Cr^{3+} - Al^{3+} - Fe^{3+} ternary diagram (Figure GS-3-6) represents the projection onto the end face of the prism; diagrams (not shown) of $\text{Cr}^{3+}/(\text{Cr}^{3+}+\text{Al}^{3+})$ and $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}^{3+}+\text{Al}^{3+})$ versus $\text{Fe}^{2+}/(\text{Mg}^{2+}+\text{Fe}^{2+})$ (i.e., $\text{Fe}\#$) represent their mutual relations to $\text{Fe}\#$. Plots (not shown) of TiO_2 against $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}^{3+}+\text{Al}^{3+})$ and against $\text{Fe}\#$ are also used to explore their compositional variations.

On the Cr^{3+} - Al^{3+} - Fe^{3+} ternary diagram, two populations of chromite are evident (Figure GS-3-6). One group displays an Fe-Ti trend and exhibits characteristics

Table GS-3-1: Chemical composition (wt. %) and structural formulas of chromite in representative samples from the Mayville intrusion and Bird River sill, Neoproterozoic Bird River greenstone belt, southeastern Manitoba.

Sample:	111-12-500B1		111-11-12		111-11-20		111-11-18		111-11-21	
Intrusion:	MI		MI		BRS		BRS		BRS	
Rock type:	Chromitite		Pyroxenite		Chromitite		Chromitite		Chromitite	
Mineral:	Chromite		Chromite		Chromite		Chromite		Chromite	
No. of grains:	4		1		8		4		4	
No. of analyses:	13		1		14		5		7	
	Av.	SD	Core	Av.	SD	Av.	SD	Av.	SD	
SiO ₂	0.01	0.01	0.16	0.02	0.01	0.03	0.02	0.07	0.11	
TiO ₂	1.17	0.06	0.50	0.44	0.20	0.36	0.04	1.26	0.04	
V ₂ O ₅	0.36	0.04	0.25	0.29	0.03	0.21	0.03	0.36	0.02	
Al ₂ O ₃	12.78	0.51	17.49	16.06	2.39	17.84	0.38	14.45	0.43	
Cr ₂ O ₃	37.22	0.29	30.81	44.37	3.62	41.57	0.25	43.02	0.90	
FeO ⁱ	44.41	0.39	43.98	28.32	2.18	30.09	1.30	30.61	3.64	
FeO	32.26	0.14	31.95	23.09	2.55	24.50	1.47	24.31	3.57	
Fe ₂ O ₃	13.50	0.31	13.37	5.81	1.22	6.22	0.24	7.00	0.21	
MnO	0.56	0.03	0.40	0.62	0.20	0.43	0.05	0.61	0.28	
MgO	1.21	0.13	0.57	6.83	1.96	6.06	0.94	6.32	2.53	
CoO	0.03	0.02	0.02	0.04	0.03	0.03	0.02	0.01	0.01	
NiO	0.08	0.03	0.00	0.09	0.06	0.12	0.03	0.14	0.03	
ZnO	0.20	0.03	0.87	0.08	0.05	0.08	0.02	0.09	0.06	
Total	99.39		96.39	97.72		97.45		97.66		
<i>On the basis of four oxygen:</i>										
Cr	1.034	0.011	0.868	1.182	0.119	1.106	0.006	1.159	0.007	
Ti	0.031	0.002	0.013	0.011	0.005	0.009	0.001	0.032	0.001	
V	0.008	0.001	0.006	0.006	0.001	0.005	0.001	0.008	0.000	
Al	0.529	0.019	0.735	0.635	0.085	0.708	0.011	0.580	0.008	
Fe ³⁺	0.357	0.009	0.358	0.147	0.029	0.158	0.006	0.180	0.008	
Fe ²⁺	0.948	0.007	0.952	0.651	0.082	0.690	0.045	0.694	0.113	
Mn	0.017	0.001	0.012	0.018	0.006	0.012	0.001	0.018	0.008	
Mg	0.063	0.007	0.030	0.341	0.091	0.304	0.045	0.319	0.121	
Co	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	
Ni	0.002	0.001	0.000	0.002	0.002	0.003	0.001	0.004	0.001	
Zn	0.005	0.001	0.023	0.002	0.001	0.002	0.000	0.002	0.001	
Cr/(Cr ³⁺ +Al ³⁺ +Fe ³⁺)	0.538	0.006	0.443	0.602	0.058	0.561	0.003	0.604	0.004	
Fe ³⁺ / (Cr ³⁺ +Al ³⁺ +Fe ³⁺)	0.186	0.005	0.183	0.075	0.015	0.080	0.003	0.094	0.004	
Al/(Cr ³⁺ +Al ³⁺ +Fe ³⁺)	0.276	0.010	0.375	0.324	0.044	0.359	0.005	0.303	0.004	
Fe ³⁺ /(Fe ²⁺ +Fe ³⁺)	0.274	0.004	0.274	0.186	0.045	0.186	0.015	0.208	0.026	
Mg/(Mg ²⁺ +Fe ²⁺)	0.063	0.007	0.031	0.343	0.088	0.306	0.045	0.314	0.116	
Fe ²⁺ /(Mg ²⁺ +Fe ²⁺)	0.937	0.007	0.969	0.657	0.088	0.694	0.045	0.686	0.116	
Cr/(Cr ³⁺ +Al ³⁺)	0.661	0.010	0.542	0.650	0.052	0.610	0.005	0.666	0.004	

Abbreviations: Av., average; BRS, Bird River Sill; Core, position of grain; MI, Mayville intrusion; SD, standard deviation

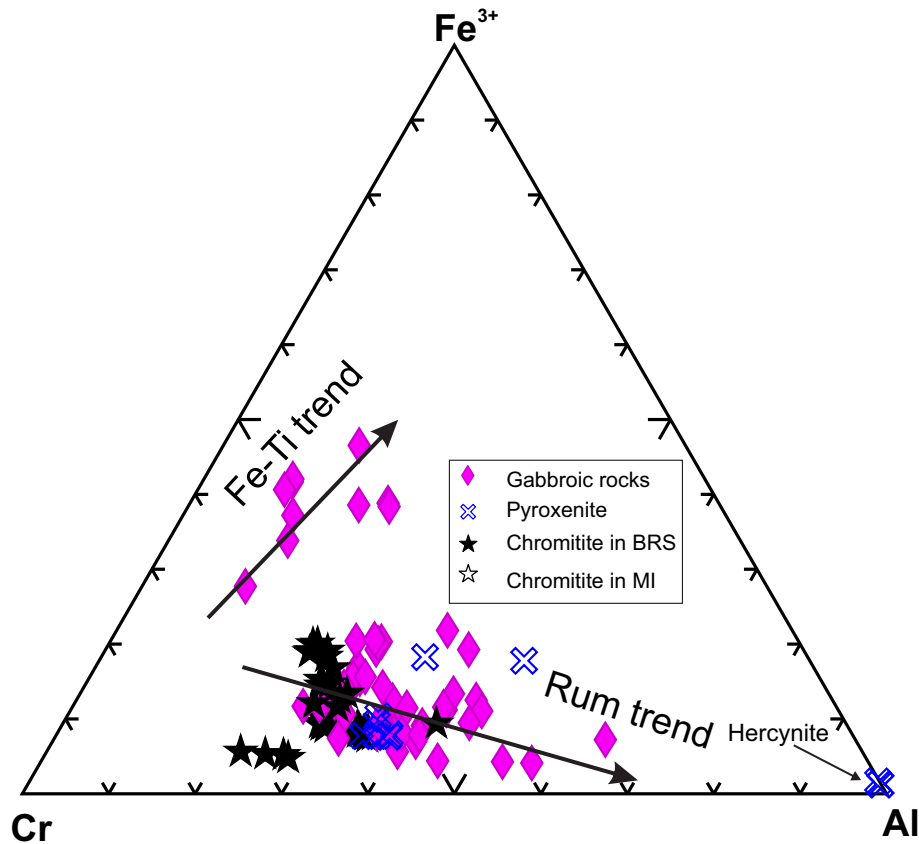


Figure GS-3-6: Ternary plot of Cr^{3+} - Al^{3+} - Fe^{3+} in chromite from the Mayville intrusion (MI) and the Bird River sill (BRS) in the Bird River greenstone belt, southeastern Manitoba. Data are from this study, Gait (1964), and Hiebert (2003). Arrows show the Fe-Ti trend and Rum trend, as defined by Barnes and Roeder (2001). The data for chromite in gabbroic rocks and pyroxenite are from the MI.

of enriched Fe^{3+} ; the other group, together with the data from the BRS, displays a Rum trend, indicating the similarity between the two intrusions in terms of chromite chemistry, although the data from the BRS lack the Fe-Ti trend. This suggests that chromite crystallized from magmas of tholeiitic affinity that may have differentiated with fractional crystallization in a continental crust setting (cf. Barnes and Roeder, 2001). It is interpreted that these combined trends are the result of reaction between cumulus chromite crystals and evolving interstitial silicate melt, consistent with the observations of Barnes and Roeder (2001). These authors pointed out that the Rum trend is commonly restricted to layered mafic intrusions and is attributed to reaction between cumulus chromite, trapped intercumulus liquid, plagioclase and olivine.

It is noted that some of the chromite in chromitite from the BRS displays relatively low Fe^{3+} contents (Figure GS-3-6). Because the ratio of chromite to the trapped silicate liquid is so high in chromitite, the effect of the reaction between chromite and interstitial liquid on the composition of chromite may be less pronounced. Thus, chromitite is more likely to reflect the primary composition of liquidus chromite.

On the plot of Cr# versus Fe# (Figure GS-3-7), chromite from the MI appears to resemble that in Archean anorthosite complexes of Rollinson et al. (2010), showing a continuous trend, but is distinctly different from that in chromitite of the BRS. The MI chromite displays variable Cr# but relatively narrow and higher Fe#. The BRS chromite, however, has relatively constant Cr# but variable and relatively lower Fe#, which may be ascribed to the late-stage metamorphic effect proposed by Scoates et al. (1986). However, it is noted that, at a fixed Cr#, the MI chromite has a higher Fe# and lower Mg# than chromite from the BRS that had formed from relatively primitive magma(s) (i.e., higher Mg#), consistent with their geochemical signatures based on bulk-rock molar $\text{MgO}/(\text{FeO}+\text{MgO})$ ratios (Yang et al., 2011, 2012). This suggests that the parental magmas of both the MI and the BRS are dominantly tholeiitic in affinity but evolved via different paths: the MI is more evolved than the BRS.

In this study, hercynite ($\text{Fe}^{2+}\text{Al}_2\text{O}_4$) was not observed from the MI, although it was reported to be present as disseminations in a pyroxenite sample by Hiebert (2003). Hercynite displays the lowest Cr# and relatively lower Fe#. This mineral belongs to a distinct population in mineral

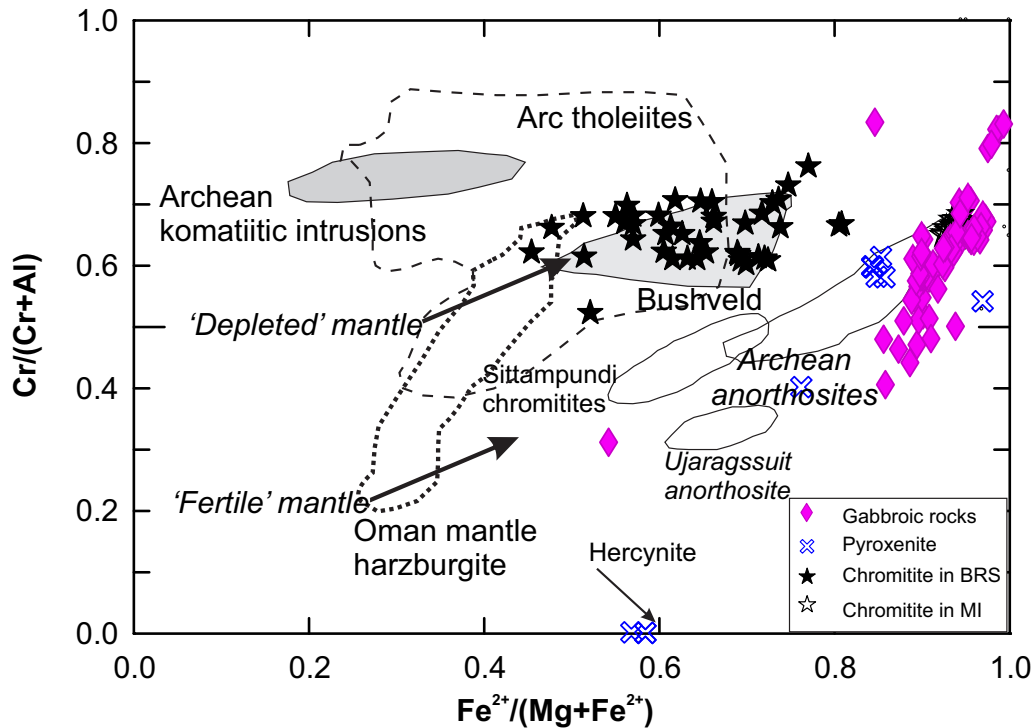


Figure GS-3-7: Plot of Fe# versus Cr# of chromite from the Mayville intrusion and Bird River sill. Data sources and symbols as in Figure GS-3-6. Hercynite has the lowest Cr# (= 0). The fields of chromite in arc tholeiite (Barnes and Roeder, 2001), the Oman ophiolite from the 'fertile' mantle harzburgite (dotted outline; Le Mée et al., 2004), and Archean komatiitic intrusions, Bushveld complex, Archean anorthosites, Ujaragssuit anorthosite and Sittampundi chromitite (Rollinson et al., 2010) are shown. The heavy arrows show the evolution of melts from aluminous (fertile) mantle in the Archean and from less aluminous (depleted) mantle in recent arcs (after Rollinson et al., 2010).

chemistry, as shown in Figures GS-3-6 and -7. The hercynite grains occur as disseminations in a matrix of amphibole and chlorite (Hiebert, 2003), suggesting that it may not be primary and perhaps formed during later alteration or metamorphism (e.g., Deer et al., 1962, 1992). Evidence of magmatic hercynite is rare (Kamenetsky et al., 2001). Thus, the possible petrogenetic implications are not discussed further here.

A diagram (not shown) of Fe# versus $Fe^{3+}/(Fe^{3+}+Cr+Al)$ indicates that the values for chromite from the MI are very low (<20 in most cases) and comparable to those from the BRS, and seem to increase with fractionation. This suggests that the parental magmas from which chromite crystallized might be relatively reduced, favouring the formation of sulphide minerals (Roeder, 1994). The Fe-numbers, however, are generally higher but less variable than those from the BRS, consistent with the conclusion that the MI is more evolved than the BRS (Yang et al., 2011, 2012). A plot (not shown) of Mg# ($Mg/(Mg+Fe^{2+})$) against $Fe^{3+}/(Fe^{3+}+Cr+Al)$ indicates that the MI chromite has much lower Mg# (<20), whereas chromite in the BRS has higher and more variable Mg# (20–50). Again, chromite from chromitite in the BRS is broadly similar to that in chromitite from continental mafic intrusions,

as compiled by Barnes and Roeder (2001), with relatively low $Fe^{3+}/(Fe^{3+}+Cr+Al)$ ratios and a range in Fe#.

Titania (wt. %) contents (not shown; see also Figure GS-3-6) increase with increasing atomic $Fe^{3+}/(Fe^{3+}+Cr+Al)$ ratios and Fe# in chromites from the MI and the BRS, a typical Fe-Ti trend commonly seen in continental mafic intrusions elsewhere, as indicated in Barnes and Roeder (2001). Chemically, chromites from these two intrusions are indistinguishable in terms of their $Fe^{3+}/(Fe^{3+}+Cr+Al)$ ratios, but the MI chromite has higher Fe#, as described above. In addition, it is noteworthy that most of the chromite has relatively low TiO_2 (<1.5 wt. %; Table GS-3-1). These values are higher than for podiform chromite (<0.3 wt. %) associated with ophiolite (e.g., Duke, 1983), but they are consistent with those crystallized from tholeiitic magmas (Kamenetsky et al., 2001) elsewhere and with the conclusions based on lithogeochemical characteristics of the MI (Peck et al., 2000, 2002; Yang et al., 2011, 2012).

It is known that trivalent (Al, Cr) and tetravalent (Ti) cations in magmatic spinel group minerals are reluctant to exchange with those in olivine during post-entrapment re-equilibration because these cations have low diffusivity in olivine compared to Mg^{2+} and Fe^{2+} . Thus, Al_2O_3 and

TiO₂ contents of spinel minerals are largely controlled by magma composition, as suggested by Kamenetsky et al. (2001), a characteristic that can be used to discriminate geodynamic settings in which the magmas formed. For example, low-Al–low-Ti spinel is related to island-arc magmas, whereas low-Al–high-Ti spinel is associated with rifting magmas in large igneous provinces. Chromites in both the MI and BRS contain relatively low Al₂O₃ and TiO₂ (Table GS-3-1), and most plot in the fields of island arc and MORB (Figure GS-3-8) with transitional features. The core compositions of chromite define a narrow range that largely straddles the boundary of island-arc magmas (ARC) and MORB, which may be compatible with a back-arc setting. According to the study of Kamenetsky et al. (2001), spinel minerals from modern back-arc environments also exhibit transitional compositions, spanning those for island arc and MORB. They suggested that back-arc magmas form in complex settings that may involve diverse melting conditions and subduction-related magma components. However, a more complicated situation is evident for the MI chromite dataset, which may be attributed to the effect of metamorphism and/or alteration. For example, Barnes (2000) and Rollinson et al. (2002) noticed that metamorphism of mid-amphibolite- to granulite-facies conditions may modify chromite chemistry, leading to enrichment in Ti⁴⁺, Fe³⁺/Fe²⁺ and Al³⁺.

It is noteworthy that Al/Mg ratios increase with decreasing Mg# in chromite from the MI and the BRS (Figure GS-3-9). This diagram shows that the MI chromite has higher Al/Mg ratios but lower Mg# than the BRS chromite, suggesting that the MI is more evolved compared to the BRS. Again, this is consistent with the prior lithogeochemical studies mentioned above, although the ultramafic unit (pyroxenite) in the MI displays a trend similar to the latter. These chemical characteristics of chromite may reflect a petrogenetic linkage between these two intrusions. Given that their ages overlap within uncertainty (i.e., MI at 2742.8 ± 0.8 Ma [Houlé et al., 2013]; BRS at 2743.0 ± 0.5 Ma [Scoates and Scoates, 2013]), they were likely produced either from partial melting of a heterogeneous mantle source or via fractional crystallization of similar parental magma derived from a subcontinental lithospheric mantle. In the former case, the MI requires a more fertile mantle source, where the BRS requires a depleted mantle source. In the latter scenario, the MI may have been sourced from a more fractionated parental magma compared to that of the BRS. Analyses showing ‘abnormal’ compositions may be attributed to the effects of metamorphism or alteration.

Hiebert (2003) concluded that the MI and BRS were probably comagmatic, in accord with the conclusions of Macek (1985). However, the compositional differences

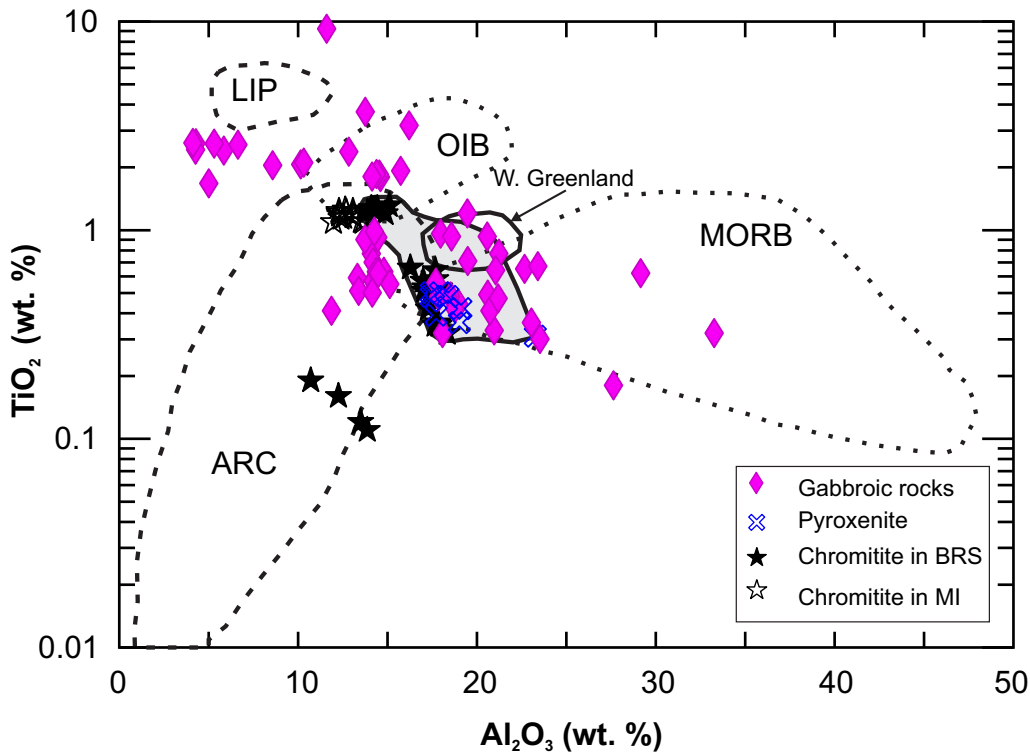


Figure GS-3-8: Plot of TiO₂ versus Al₂O₃ contents (wt. %) in chromites from the Mayville intrusion and Bird River sill. The shaded area denotes core compositions. The discrimination fields of chromian spinel inclusions trapped in primitive olivine (Fo > 84) from mid-ocean-ridge basalt (MORB), oceanic-island basalt (OIB), large igneous provinces (LIP), island-arc magmas (ARC) and west Greenland are from Kamenetsky et al. (2001). Data sources and symbols as Figure GS-3-6.

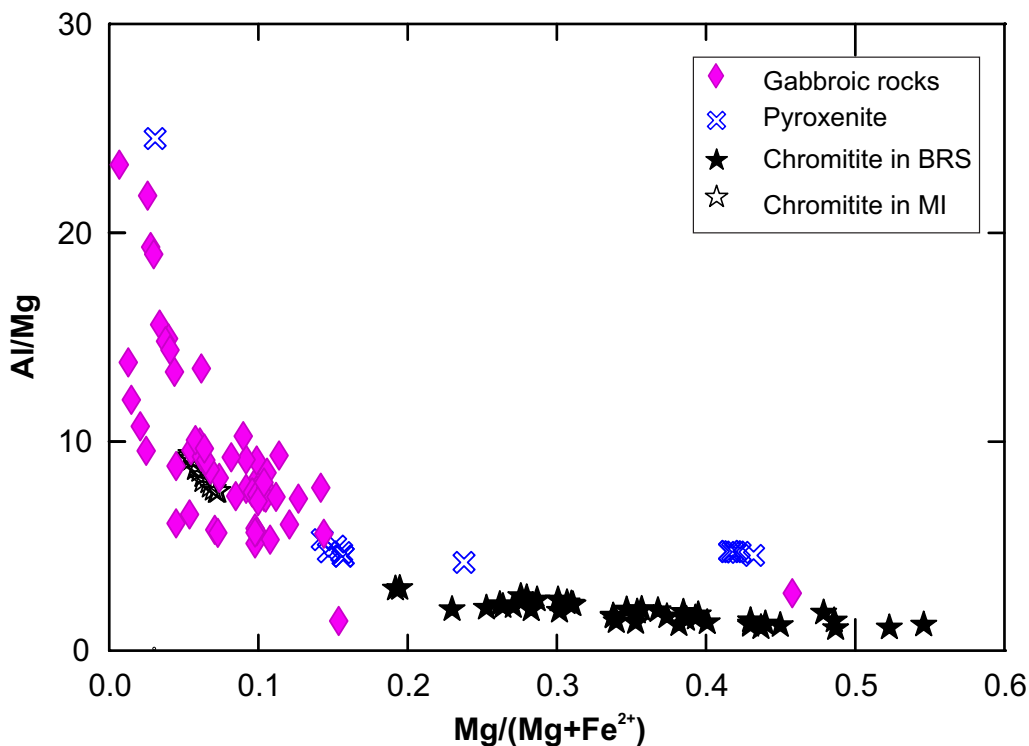


Figure GS-3-9: Plot of Al/Mg versus Mg# ($Mg^{2+}/[Mg^{2+}+Fe^{2+}]$) in chromite from the Mayville intrusion (MI) and Bird River sill (BRS). Data sources and symbols as Figure GS-3-6.

between the two chromite populations suggest minor differences in magmatic processes.

Minor oxides V_2O_5 , NiO, CoO, ZnO and MnO in chromite were also analyzed in this study, but no anomalous values were noted (Table GS-3-1), although the MI chromite exhibits relatively lower NiO contents than the BRS. This relative depletion of Ni in the MI chromite suggests that it is prospective for magmatic Ni mineralization (e.g., Barnes and Tang, 1999).

Discussion

Three mechanisms have commonly been cited to explain crystallization of chromite from a mafic-ultramafic magmatic system to form chromitite seams or layers: fractional crystallization, contamination by silic material and magma mixing (Irvine, 1975, 1977; Marques et al., 2003). Elevation of oxygen fugacity (fO_2) may also trigger chromite precipitation (Ulmer, 1969). Talkington et al. (1983) suggested that increasing fO_2 could occur by wallrock assimilation or new magma injection. Liquid immiscibility was also proposed for the origin of chromitite seams in layered mafic-ultramafic intrusions (McDonald, 1965).

In the Chromitiferous zone of the BRS (Figures GS-3-4, -5a), chromite appears to have crystallized after olivine. Fractional crystallization of olivine drove the melt composition toward the olivine-chromite cotectic line, where chromite coprecipitated with olivine until

the appearance of orthopyroxene. This model is consistent with field investigations and petrography (Scoates et al., 1986, 1989), which document olivine cumulates at the base, olivine-chromite cumulates in the middle, and chromitite (chromite cumulates) and pyroxene cumulates at the top of each igneous unit. Alternatively, fresh primitive magma fluxing into the magma chamber and mixing with evolving magmas could result in chromite crystallization and formation of chromitite layers (e.g., Irvine, 1977; Scoates et al., 1989). Field relationships are consistent with the scenario of multiple injections of magma having taken place within the BRS (Mealin, 2008), which is a composite intrusion similar to the MI in this regard.

Crystallization of calcic plagioclase (Yang, unpublished data, 2013) resulted in alumina depletion and chrome build-up in the magmatic systems that contain up to 5% water, depending upon pressures suggested in the experimental study of Takagi et al. (2005). Thus, at the chromitite stage, chromite crystallized from mafic-ultramafic magma(s) relatively poor in Al_2O_3 but rich in mafic components. Crystallization of chromite led to the magma gradually becoming enriched in Al but depleted in Mg, reflecting a decrease of Mg# and an increase of Al/Mg ratio in the MI chromite (Figure GS-3-9).

The chemistry of chromite, lithogeochemistry and experimental constraints require a hydrous, high-Al tholeiitic magma(s) parental to the MI. The magma reached liquidus with cooling, and started to crystallize

calcicplagioclase, then plagioclase+chromite, plagioclase+chromite+amphibole (after pyroxene) and chromite+amphibole (after pyroxene). Recrystallization of plagioclase may have occurred during later deformation and greenschist to amphibolite metamorphism to produce a granular texture within former megacrysts, similar to what is observed in the Fiskenæsset anorthositic complex of west Greenland (Windley and Garde, 2009; Rollinson et al., 2010).

Chromite may form distinct bands due to crystal sorting and accumulation, or igneous sedimentation processes, in a layered mafic–ultramafic intrusion; if sufficiently concentrated, a chromite deposit could form, as evidenced by the BRS and the Euclid Lake intrusion (Watson, 1985).

Further work is required for the MI and BRS chromites, as they may be used to estimate intracrystalline closure temperatures (T_c ; Princivalle et al., 1999; Lenaz et al., 2004, 2011; Lucchesi et al., 2010) and fO_2 (Ballhaus et al., 1991). Such work may provide more information on the cooling rate of these intrusions and factors controlling the formation of sulphide minerals and chromitite.

Economic considerations

The Mayville intrusion (MI) is a composite mafic–ultramafic intrusion that was emplaced broadly coeval with the Bird River sill (BRS). These intrusions are attributed to the Neoproterozoic ‘Bird River magmatic event’ (Houlé et al., 2013), which is associated with several significant deposits of magmatic Ni-Cu-PGE and Cr in Manitoba and along strike to the east in Ontario (i.e., the ‘Ring of Fire’). Mineral resources in the MI were recently updated by Mustang Minerals Corp. to include 26.6 Mt grading 0.18% Ni, 0.44% Cu and 0.24 g/t combined Pt+Pd+Au in the indicated category, and 5.2 Mt at similar grade in the inferred category (Mustang Minerals Corp., 2014). The Bird River chromite deposit includes an historical resource of 60 Mt grading 3.88% Cr_2O_3 (Watson, 1985), which represented the major repository of chromite resource in Canada prior to the discovery of the McFaulds Lake deposits (i.e., the Ring of Fire) in northern Ontario.

In this study, chromite chemistry is used as a ‘petrogenetic indicator’ to investigate the nature of mafic–ultramafic magmas parental to the MI and the BRS, their possible magmatic evolution and the potential tectonic setting of the Bird River greenstone belt, and to provide insights into several key aspects relevant to exploration for magmatic Ni-Cu-PGE-(Cr) deposits, such as affinity (nature) and fertility of magmas, processes of magmatic evolution and regional tectonic setting. These new data can help to determine where and why magmatic Ni-Cu-PGE-Cr mineralization occurs, but they must be used in conjunction with detailed geological mapping and litho-geochemistry. Chemical compositions of MI chromite indicate that the parental magma(s) is/are tholeiitic and

may have been derived from subcontinental lithospheric mantle enriched by slab melts with tonalite, trondhjemite and granodiorite affinity (the slab melt may be represented by the quartz diorite–tonalite dikes cutting the heterolithic breccia zone, as shown in Figure GS-3-2) due to plate subduction. This scenario was also proposed by Rollinson et al. (2010) for the genesis of the Archean anorthosite suite in western Greenland. The MI is considered favourable for magmatic Ni-Cu-PGE-(Cr) mineralization, given that it was emplaced into suitable supracrustal rocks, such as the sulphide-bearing metasedimentary rocks to the north, that might provide the external sulphur required for sulphur saturation and precipitation of sulphide.

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