



# Formation and evolution of the chromitites of the Stillwater Complex: a trace element study

Philippe Pagé, Sarah-Jane Barnes

Canada Research Chair in Magmatic Metallogeny, Université du Québec à Chicoutimi, 555 Bld de l'Université, Saguenay, Québec, Canada, G7H 1B2

Michael L. Zientek

U.S. Geological Survey, Spokane, Washington, U.S.A.

**Abstract.** Large layered intrusions, such as the Stillwater Complex, contain cyclic units of chromite-rich layers (cm to m thick) having kilometre-scale lateral extension. Chromite cumulates are among the first to form after new primitive melt injections into the magma chamber. Therefore, chromite cumulates could be used to investigate the nature of the parental magma, given the fact that chromite preserves its primary original magmatic composition. The cooling and crystallization history of large layered intrusions is long, complex, and involves multiple injections of hot primitive magma into an evolving and fractionating magma chamber. Our study on Stillwater chromites shows that the early crystallized chromite experiences various post-cumulus processes with the interstitial silicate melt, such as the precipitation of chromite overgrowths on early formed cumulus chromite and/or the reaction - reequilibration of early formed cumulus chromite. These processes have modified the primary magmatic composition of the chromite making it difficult to identify the parental magma. Moreover, mineralogical evidence for chromite - interstitial melt interactions have probably been obliterated during late post-magmatic textural maturation and recrystallization which tends to homogenize chromite grain size and composition.

**Keywords.** chromite, Stillwater Complex, LA-ICPMS trace element, crystal-melt interaction, parental melt

## 1 Introduction

It is well-known that large layered igneous complexes, such as Stillwater (U.S.A.), Bushveld (South Africa), Great Dyke (Zimbabwe) and Muskox (Canada) among others, contain, within their ultramafic parts, cyclic units of chromite-rich layers (cm to m thick) which extend laterally up to several kilometres. These stratiform chromitites form layers of primary magmatic crystals of chromite precipitated at an early stage after new primitive melt injections in the magma chamber and accumulated on the floor of the magma chamber. Since chromite is one of the first phases to crystallize in ultramafic - mafic silicate melts, our aim was to use the major and trace element signature of chromite from chromitites to investigate the nature of the Stillwater Complex (SC) parental magma, which is not well constrained at present. This technique has been successfully applied to ophiolitic podiform chromitites (Pagé and Barnes 2009), but could it be applied to large layered complexes?

The cooling and crystallization history of large layered intrusions is complex and involves multiple

injections of hot primitive magma into an evolving and fractionating magma chamber. The chromite-cumulate layers are subject to experience various early post-cumulus processes with the interstitial silicate melt which may have modified the primary magmatic composition of chromite. So, before the complete solidification of the cumulate pile, a portion of the residual melt interstitial to the cumulate crystals will migrate upwards during compaction of the cumulate pile (filter pressing), which greatly increases the melt : chromite crystal ratio (Irvine 1980).

Overgrowths of chromite can precipitate from the interstitial melt on early formed cumulus chromite, or cumulus chromite can react and reequilibrate with the interstitial melt as other phase(s) are crystallizing; both processes reduce porosity as a side effect (Barnes 1986). It is inevitable that during crystallization and reduction of the porosity the chromite composition can be significantly modified depending i) on the proportion of chromite in the rock and the nature of the co-existing silicates phases (e.g., pyroxene or plagioclase) which will compete for certain elements, ii) on the interstitial melt to cumulus (chromite) crystal ratio, and iii) on the cooling rate (Hunter 1987).

Also, at a post-magmatic sub-solidus stage, the magmatic textures will recrystallize to variable degrees (textural maturation) according to the cooling rate of the cumulate pile. These post-cumulus textural maturation and recrystallization processes tend to homogenize the grain size and the chemistry of chromite crystals (Hunter 1987).

In order to characterize the primary magmatic composition of chromite and to investigate the effects of post-cumulus magmatic processes that may have occurred during the evolution and solidification of the ultramafic part of the SC magma chamber, we have determined the major and trace elements (Cr, Al, Fe, Mg, and Ti by microprobe; Sc, V, Mn, Co, Ni, Zn, and Ga by laser ablation ICP-MS) of chromite from the chromitite layers of the SC. Our ultimate goal is to identify the nature of SC parental magma.

## 2 Geological setting and samples

### 2.1 The Stillwater Complex (SC)

The Stillwater layered igneous Complex consists of a large (~6 by 48 km) ultramafic to mafic intrusion emplaced during the Archaean (~2700 Ma; Premo et al. 1990) into existing metasedimentary rocks. The five

major subdivisions of the SC comprise, from the base to the top, the Basal Series, the Ultramafic Series, and the Lower, Middle, and Upper Banded Series. The Ultramafic Series have been subdivided into a lower Peridotite Zone, containing all the major chromitite layers, and an upper Bronzite Zone (Zientek et al. 1985). In the Ultramafic Series, plagioclase together with amphibole and phlogopite are present but only as late intercumulus phases.

Depending on the location of traverses along the SC, the Peridotite Zone consists several cyclic units (8 to 24) having an idealized sequence, from the base to the top, of olivine cumulate, olivine-bronzite cumulate, bronzite-olivine cumulate and bronzite cumulate (Jackson 1961). In the sampled sections, fifteen cyclic units contain chromitite layers within their olivine cumulate part. Chromitite layers show variations in their thickness and their modal proportions making correlations from place to place somewhat difficult. The larger chromitite layers can reach more than 1 m thick, and comprise many massive layers and lower grade olivine-chromite cumulate intervals. They can extend for more than 20 km along strike (Jackson 1961).

## 2.2 The studied samples

We have analysed chromite from 29 chromite-rich rocks from the basal parts of 10 magmatic cyclic units sampled in the Mountain View and Benbow areas, on the east side of the SC. The studied samples range from i) chromite-rich olivine-cumulate to olivine-rich chromite-cumulate with ~8 <70% euhedral to rounded disseminated interstitial chromite (net texture) to semi-massive chromitites. These samples can contain ~15-25% of intercumulus material dominated by pyroxene and plagioclase, sometimes showing poikilitic to sub-pegmatitic habits, and minor hydrous phases to ii) massive chromitites (70 - 80% chromite) to very massive chromitites (85 - 98% chromite). Orthopyroxene, clinopyroxene, plagioclase and hydrous phases are interstitial to chromite.

## 3 Methodology and observations from LA-ICPMS analysis of chromite

The major element composition of chromite was determined by microprobe CAMECA SX100 with wavelength dispersive mode at Université Laval (Québec City). Details of the methodology have been presented elsewhere (Pagé and Barnes 2009).

The minor and trace element contents of chromite were determined by LA-ICP-MS at the Université du Québec à Chicoutimi following the methodology of Pagé and Barnes (2009) and Pagé et al. (in press). The LA-ICP-MS system used is a Thermo X7 ICP-MS coupled with a New Wave Research 213 nm UV laser. In addition to the trace elements analysed (<sup>45</sup>Sc, <sup>51</sup>V, <sup>55</sup>Mn, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>68</sup>Zn, and <sup>69</sup>Ga), other elements / isotopes (<sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>34</sup>S, <sup>44</sup>Ca, <sup>46</sup>Ti, <sup>47</sup>Ti, <sup>49</sup>Ti, <sup>53</sup>Cr, <sup>57</sup>Fe, <sup>61</sup>Ni, <sup>65</sup>Cu, <sup>71</sup>Ga, <sup>77</sup>Se, <sup>82</sup>Se, <sup>88</sup>Sr, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>101</sup>Ru, <sup>103</sup>Rh, <sup>105</sup>Pd, <sup>115</sup>In, <sup>118</sup>Sn, <sup>192</sup>Os, <sup>193</sup>Ir, and <sup>195</sup>Pt) were monitored during chromite ablation to control the nature of the ablated

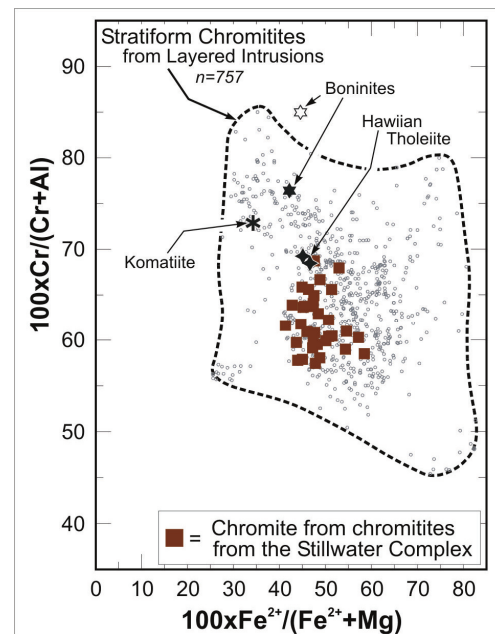
material and the presence of included phases, and to verify their presence/abundance in chromite. Analytical results from in-house monitor indicate that the relative standard deviation is 4 to 20 percent.

The majority of ablation profiles are free of any inclusions. However, silicates (Si, Ca, ± Sr, and ± Y peaks), sulphides (Cu and ±Rh, ±Ru), or PGM (Os, Ir, Ru, ± Rh) were rarely encountered.

## 4 Chemical composition of chromite from Stillwater Complex chromitites

### 4.1 Major elements

Chromite from the SC chromitites have Cr# [100Cr/(Cr+Al)] ranging from 57.4 to 68.7 and Fe<sup>2+</sup># [100Fe<sup>2+</sup>/(Fe<sup>2+</sup>+Mg)] ranging from 41.3 to 58.5, and they plot within the field of chromite from chromitites from layered intrusions (Fig. 1). In detail, the chromite from SC chromitites tend to plot on the Mg-rich side of the largest concentration of data, and our results do not show any particular trend that can be clearly related to the effect of simple fractional crystallization of chromite.



**Figure 1.** Cr# and Fe<sup>2+</sup># ratios of chromites from Stillwater Complex stratiform chromitites compared to the compositional field of chromite from chromitites from layered intrusions (Barnes and Roeder 2001).

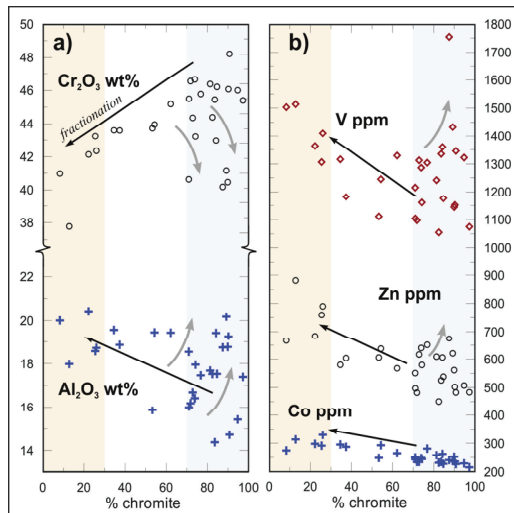
### 4.2 Trace elements

The eight transition metals (Sc, Ti, V, Mn, Co, Ni, Zn, and Ga) are above detection level (DL varying from 0.02 to 1 ppm). However, all of the following elements are below detection levels: Si < 60 ppm, Ca < 40 ppm, Ge, Se, Zr, Mo, Ru, Cd, In, Sn (0.01 < DL < 0.1 ppm) and Y, Nb, Ag, W, Re, Os, Ir, Au (0.001 < DL < 0.01 ppm).

### 4.3 Chemical variation with chromite content

The composition of the chromite varies with the modal proportion of chromite within the samples (Fig. 2). The decreasing Cr and increasing Al contents of chromite as the proportion of chromite decreases (Fig. 2a) can be interpreted as a trend of fractional crystallization (early Cr-rich massive chromitites evolve towards late relatively Cr-poor Al-rich disseminated chromite). However, at high chromite fraction (>70%) trends get more diffuse and complex for most of the elements suggesting that fractional crystallization is not the only process influencing the composition of the chromites of the SC chromitites.

The trends illustrated for the trace elements (Fig. 2b) suggest that the amount of chromite is important in controlling chromite composition with V, Zn and Co increasing during fractionation. Again some complexities and discrepancies between major and trace elements are observed for the more massive samples.



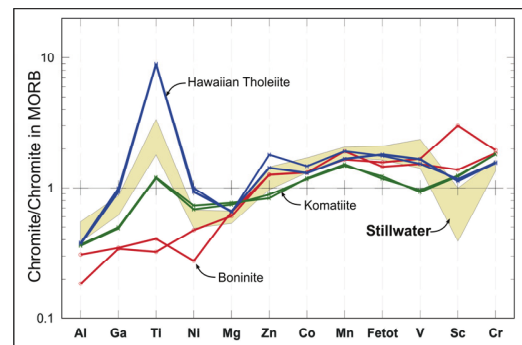
**Figure 2.** Variations of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> (a) and of V, Zn and Co (b) contents of chromite with modal proportion of chromite in the Stillwater Complex chromitites.

However, the negative correlation between trace element content in chromite and its proportion in the rock can also be considered as the result of melt - chromite reaction. As the chromite proportion decreases in the rock, the buffering effect related to its proportion decreases as well as allowing chemical components from a large volume of melt to react with a small volume of chromite, and vice-versa.

## 5 Stillwater Complex parental magma

In order to constrain better the nature of the SC parental magma, we have plotted the compositions of chromites from massive chromitites compared to chromite from various ultramafic to mafic lavas (Fig. 3). The chemical profiles of the SC chromites are significantly different from the chromites from komatiite, boninite, and Hawaiian tholeiite. This indicates that either these particular types of melts are not involved in forming the

Stillwater Complex, or that the primary magmatic signature of chromite grains have been variably reequilibrated with migrating interstitial melt at a post-cumulus stage. Mineralogical evidence for chromite - interstitial melt interactions have probably been obliterated during post-magmatic textural maturation and recrystallization.



**Figure 3.** Composition of chromites from the Stillwater Complex massive chromitites compared to chromite from ultramafic-mafic volcanic rocks, including komatiite, boninite, and Hawaiian tholeiite, all of which have been normalised to the composition of the chromite from the MORB.

## Acknowledgements

We thank D Savard at UQAC for his assistance during LA-ICP-MS work and S. Dare for proof reading the English. This project is funded by the Canadian Research Chair in Magmatic Metallogeny.

## References

- Barnes SJ (1986) The effect of trapped liquid crystallization on cumulus mineral compositions in layered intrusions. *Contrib Mineral Petr* 93:524-531
- Barnes SJ, Roeder PL (2001) The range of spinel compositions in terrestrial mafic and ultramafic rocks. *J Petrol* 42:2279-2302
- Hunter RH (1987) Textural equilibrium in layered igneous rocks. In: Parsons I (ed) *Origins of Igneous Layering*. NATO ASI Series C196:473-503
- Irvine TN (1980) Magmatic infiltration metasomatism, double-diffusive fractional crystallization, and adcumulus growth in the Muskox Intrusion and other layered intrusions. In: Hargraves RB (ed) *Physics of Magmatic Processes*. Princeton, NJ: Princeton University Press, pp 325-383
- Jackson ED (1961) Primary textures and mineral associations in the Ultramafic zone of the Stillwater Complex. USGS Professional Paper 358:106 p
- Pagé P, Barnes S-J (2009) Trace elements signature of chromites from podiform chromitites of the Thetford Mines Ophiolite, Québec, Canada: products of boninitic melt migration. *Econ Geol* 104:997-1018
- Pagé P, Barnes S-J, Bédard JH, Zientek ML (*in press*) Are Os, Ir, and Ru controlled by chromite? Results from plutonic and volcanic rocks. *Chem Geol*
- Premo WR, Helz RT, Zientek ML, Langston RB (1990) U-Pb and Sm-Nd ages for the Stillwater Complex and its associated sills and dikes, Beartooth Mountains, Montana. Identification of a parent magma? *Geology* 18:1065-1068
- Zientek ML, Czamanske GK, Irvine TN (1985) Stratigraphy and nomenclature for the Stillwater Complex. In: Czamanske GK, Zientek ML (eds) *The Stillwater Complex, Montana: geology and guide*. Montana Bur Min Geol Spec Pub 92:21-32