

Genesis of chromite deposits by dynamic upgrading of Fe ± Ti oxide xenocrysts

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ABSTRACT

Most magmatic chromite deposits, particularly those in stratiform layered ultramafic intrusions, are interpreted to have formed by processes that decrease the solubility of chromite. However, such models have difficulty in explaining the great thicknesses (up to 10 m) of chromite mineralization at Inyala and Railway Block (Zimbabwe), Ipueira-Medrado (Brazil), Uitkomst (South Africa), and Sukinda (India), and the very great (up to 100 m) thicknesses of chromitite at Kemi (Finland) and in the Black Thor Intrusive Complex (Canada). We propose a new process that involves partial melting of Fe ± Ti oxide-rich rocks (oxide-facies iron formation or ferrogabbro) and conversion of fine-grained oxide to chromite by reaction with Cr-rich komatiitic magma in a dynamic magma conduit. This process is analogous to the widely accepted model for the upgrading of barren iron-sulfide xenomelts to form magmatic nickel-copper-platinum group element deposits. We demonstrate that this process is geologically, physically, and chemically feasible, that it probably occurred in the Black Thor Intrusive Complex, and that it may have applications elsewhere.

INTRODUCTION

Chromite deposits have traditionally been subdivided into stratiform (type I) and podiform (type II) types (e.g., Stowe, 1994). However, it has become clear that type I stratiform deposits can be subdivided (Prendergast, 2008) into those hosted by large, differentiated layered intrusions (periodically replenished magma chambers) (type IA), and small, less-differentiated magmatic conduits (flow-through feeder conduits and/or sills) (type IB) (Table DR1 in the GSA Data Repository¹). Type IB deposits are normally laterally less extensive but thicker than type IA deposits, are typically hosted by more ultramafic rocks, are ordinarily derived from more magnesian—commonly komatiitic—magmas, and usually have higher Mg and lower Al contents (Table DR1).

A fundamental problem in the genesis of all stratiform chromite deposits is how layers of massive to semi-massive chromite that are commonly up to 1 m thick (e.g., Bushveld [South Africa], Stillwater [Montana, USA]), less

commonly up to 10 m thick (e.g., Inyala and Railway Block [Zimbabwe], Ipueira-Medrado [Brazil], Uitkomst [South Africa], Sukinda [India]), but in some cases up to 100 m thick (e.g., Kemi [Finland], Black Thor Intrusive Complex [Canada]) (Table DR1) are generated from magmas that typically contain <0.35% Cr and crystallize very small amounts of chromite (normally <1% of the cumulus assemblage). Many models have been suggested, including (1) liquid immiscibility (e.g., McDonald, 1965), (2) oxidation (e.g., Ulmer, 1969; Ferreira Filho and Araujo, 2009), (3) felsification (e.g., Irvine, 1975; Spandler et al., 2005), (4) magma mixing (e.g., Irvine, 1977; Campbell and Murck, 1993), (5) pressure increase (e.g., Cameron, 1980; Lipin, 1993) or decrease (Latypov et al., 2018), (6) assimilation of iron formation (e.g., Rollinson, 1997), (7) hydration (e.g., Azar, 2010; Prendergast, 2008), (8) dynamic crystallization (Yudovskaya et al., 2015), and (9) cumulate-melt interaction (e.g., O'Driscoll et al., 2010), with or without upward transport (e.g., Eales,

2000; Mondal and Mathez, 2007) and/or downward slumping (e.g., Maier et al., 2013).

These processes are not mutually exclusive and may have operated to varying degrees in different deposits, yet all have problems. Upward-transport models simply relocate the problem, add a major degree of fluid dynamic complexity in terms of requiring re-entrainment of previously segregated chromite, and do not explain why chromite does not occur in economic concentrations in volcanic rocks. Magma mixing, contamination, oxidation, hydration, and pressure changes all are feasible to varying degrees, but require the amount of magma to greatly exceed the thickness of the host intrusion (e.g., Campbell and Murck, 1993; Eales, 2000; Carson et al., 2013). Layered intrusions likely inflated during crystallization and never contained melt zones of the thicknesses required at the lower (more realistic) efficiencies of extraction. Phase-equilibria studies (e.g., Irvine, 1977; Murck and Campbell, 1986) indicate that the most popular model—mixing of parental (new influx) and fractionated (resident) magmas across the convex olivine-chromite cotectic to drive it into the volume of chromite-only crystallization—can generate only ~0.1 wt% chromite as the magma is driven back to the cotectic. The interval over which chromite alone can crystallize after a pressure decrease (Latypov et al., 2018) has not been established, however it is limited within this context by the low solubility of Cr in silicate magmas.

Crystallization and deposition of chromite in a flow-through system, analogous to the lava channels and magma conduits that host magmatic Ni-Cu-platinum group element (PGE) deposits (e.g., Leshner et al., 1984; Leshner, 1989; Arndt et al., 2008), which are inferred to

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¹GSA Data Repository item 2019075, Table DR1 (classification of Type I stratiform magmatic chromite deposits) and Table DR2 (key characteristics of Type IB conduit-hosted chromite deposits), is available online at <http://www.geosociety.org/datarepository/2019/>, or on request from editing@geosociety.org.

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have processed two to three orders of magnitude more magma than the amount of sulfide presently preserved in the channels, would solve the mass-balance problem. However, the process(es) required to drive the magma into the field of chromite-only crystallization would need to occur continuously over very long periods of time to generate the vast amounts of chromite in type IB deposits.

Wholesale assimilation of iron formation (Rollinson, 1997) explains the close association of many type IB deposits with iron formation (Table DR2), however there are several problems with such a process:

(1) The presence of cotectic olivine(-chromite) cumulate rocks in the lower parts of the host intrusions (e.g., Kemi: Alapieti et al., 1989; Black Thor: Carson et al., 2013) indicates that the magmas were already saturated in chromite, so they should not have been able to assimilate another oxide phase.

(2) Adding an assimilate containing >20% FeO to a komatiitic magma that would normally contain ~10%–12% FeO would increase the Fe/Mg ratios of olivine, orthopyroxene, and clinopyroxene, which does not appear to be observed (e.g., Azar, 2010).

(3) Assimilation-crystallization models indicate that the modal proportion of chromite generated by such a process would be <0.3% (Azar, 2010).

PARTIAL MELTING AND UPGRADING

A solution to this problem would be for the parental magma to partially melt an oxide-rich lithology such as oxide-facies iron formation or ferrogabbro. A high-Mg komatiitic magma with ~30% MgO would be undersaturated in chromite (Murck and Campbell, 1986) and would be able to completely assimilate significant amounts of either lithology; however, a low-Mg komatiitic magma with ~20% MgO would be saturated in chromite and would be able to dissolve the silicate phases but not the oxide phases. Addition of silica would account for the abundance of orthopyroxene in magmas that normally crystallize clinopyroxene (Arndt et al., 2008).

Converting xenocrystic magnetite and/or ilmenite to chromite requires magnetite to incorporate Cr-Al-Mg-V-Ni from the magma and release Fe and/or Ti into the magma. Magnetite and chromite are both isometric, so the conversion from magnetite would be topotactic, whereas ilmenite is trigonal, so the conversion from ilmenite would require a structural inversion, however that is unlikely to be a barrier at such high temperatures.

Whether this process is completely diffusional or whether it involves crystallization of additional chromite around the xenocryst depends on the enthalpy of the system, which depends on the relative rates of thermomechanical erosion, assimilation, and crystallization (see,

e.g., Williams et al. 1998); however, the amount of magma required can be calculated from mass balance (Leshner and Burnham, 2001):

$$Y_i^f = \frac{(X_i^o R + Y_i^o)}{R + D_i^{\text{oxide/melt}}}, \quad (1)$$

where X_i^o is the concentration of element i in the initial silicate magma, Y_i^o is the concentration of i in the initial oxide (magnetite or ilmenite), Y_i^f is the concentration of i in the final oxide (chromite), $D_i^{\text{oxide/melt}}$ is the oxide-silicate melt partition coefficient for element i , and R is the magma/oxide mass ratio. Using conservative abundances of Cr in the magma and reasonable partition coefficients for Cr and Ti, the results (Fig. 1) indicate that magma/oxide ratios as low as 100 can produce Cr-rich chromites. These values are on the low end of estimates of R for many komatiitic Ni-Cu-(PGE) systems (e.g., 100–500 for Kambalda [Western Australia]: Leshner and Campbell, 1993; 300–1100 for Raglan [Canada]: Barnes and Picard, 1993; 50–200 for Thompson [Canada]: Layton-Matthews et al., 2011), so should be achievable in the dynamic systems envisioned for type IB chromite deposits.

This process is also limited by the diffusion rates of Cr-Al into magnetite/ilmenite and Ti out of ilmenite. The chromite grains in the best-preserved deposits are typically 0.1–0.2 mm, the magnetite grains in ferrogabbros are typically similar, and the magnetite grains in weakly metamorphosed iron formations are ~0.002 mm.

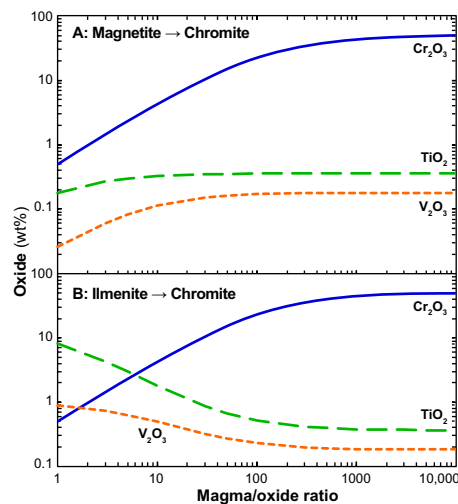


Figure 1. Variations in the abundances of Cr, Ti, and V in oxide composition as function of magma/oxide mass ratio. Calculation method is described in text. **A:** Model for converting magnetite to chromite, assuming 0.5% Cr_2O_3 , 0.36% TiO_2 , and 0.03% V_2O_5 in initial magma, and $D_i^{\text{oxide/magma}}$ (partition coefficient) of 100 for Cr, 1 for Ti, and 6 for V (estimated from observed compositions), and no Cr, Ti, or V in initial oxide (typical magnetite in iron formation). **B:** Model for converting ilmenite to chromite. Same as A except assumes 16% TiO_2 and 1% V_2O_5 in initial oxide (typical titanomagnetite in ferrogabbro).

We have estimated the amount of time required to diffuse Cr-Al-Ti from a magma kept at constant composition (through advective flow) to the core of a 0.1 mm magnetite grain initially containing no Cr-Al-Ti using a one-dimensional (1-D) analytical solution to Fick's second law of diffusion (equation 2.45 in Crank, 1975), modified to allow for the preferential partitioning of Cr-Ti-Al from the melt into the oxide phase:

$$C_{(x,t)} = C_o D^{\text{oxide/magma}} \operatorname{erfc} \frac{x}{2\sqrt{Dt}}, \quad (2)$$

Where $C_{(x,t)}$ is the concentration of Cr in the magnetite at distance x from the rim at time t , C_o is the concentration of Cr in the magma (assumed to be 3500 ppm in this case), $D^{\text{oxide/magma}}$ is the oxide-magma partition coefficient, erfc is the complementary error function, and D is the diffusion constant at 1440 °C, a temperature appropriate for a 22% MgO komatiitic magma. There are more sophisticated 2-D and 3-D solutions, but given all of the uncertainties in parameterization and the isometric structures of magnetite and chromite, the 1-D calculation is sufficient to demonstrate the feasibility of the process. The results (Fig. 2) indicate that 0.1 mm magnetite or ilmenite grains could be completely converted to chromite in 1–10 days, much less than the weeks to years duration of single magmatic events and the thousands to millions of years duration of most magmatic systems. This is consistent with the observation that individual chromite grains

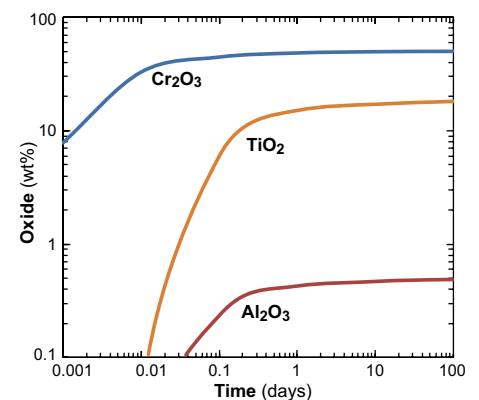


Figure 2. Calculated abundances of Cr-Al-Ti diffused into core of 0.1-mm-diameter magnetite grain. Calculation method is described in text. Cr exchange is essentially complete after 1 day, and Al and Ti after 10 days. Calculation assumes 0.5% Cr_2O_3 , 9% Al_2O_3 , and 0.5% TiO_2 in magma (estimated based on observed compositions); $D_i^{\text{oxide/magma}}$ (partition coefficient) of 100 for Cr, 2 for Al, and 1 for Ti (based on observed compositions); D_o (pre-exponential diffusion factor) of $7.17 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ for Cr, 1.46×10^{-5} for Al, and 2.77×10^{-5} (Dieckmann et al., 1978; Aggarwal and Dieckmann, 2002); Q (activation energy for diffusion) of 335 kJ mol^{-1} for Cr, 265 kJ mol^{-1} for Al, and 267 kJ mol^{-1} for Ti (Dieckmann et al., 1978; Aggarwal and Dieckmann, 2002); and T (temperature) of 1440 °C (appropriate for a 22% MgO magma).

in most deposits are unzoned or normally zoned (reflecting equilibration with trapped liquid and/or modification during serpentinization).

DISCUSSION

The Black Thor and Double Eagle Intrusive Complexes in the Ring of Fire Intrusive Suite of northern Ontario (Canada) appear to have had the best opportunity to generate chromite mineralization by the proposed mechanism. There are oxide-silicate-facies iron formations and Fe-Ti oxide-bearing gabbros in underlying rocks, the intrusions contain iron-formation and gabbro xenoliths, the parental magma was a chromite-saturated low-Mg komatiite (Mungall et al., 2010), and the chromite-bearing intrusions are dominated by cumulates and interpreted to represent flow-through magma conduits (Carson et al., 2013). The chromites in the Black Thor Intrusive Complex exhibit a wide range of textures including (1) massive, (2) inclusion-bearing (predominantly serpentine-actinolite-chlorite interpreted to represent altered komatiitic melt inclusions), and (3) pitted with fine Fe ± Cu sulfides (Fig. 3A). The first and third are similar to the textures of magnetite-silicate±sulfide

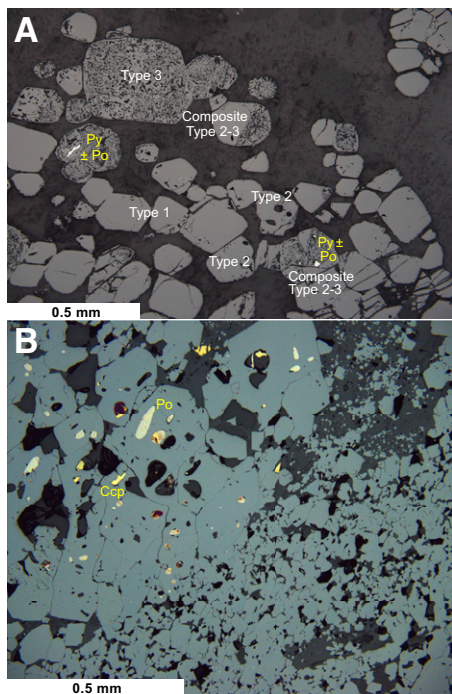


Figure 3. A: Backscattered electron image of chromites (gray) in Black Thor Intrusive Complex (Canada: Universal Transverse Mercator coordinates 551333 m E, 5845928 m N, Zone 16, NAD83 datum) showing type I (massive), type II (inclusion-bearing), and type III (pitted) textures, including some composites of those types. Sample 1331337, DDH BT-09-76, 186 m. **B:** Photomicrograph of magnetite-silicate ± sulfide-facies iron-formation within the foot-wall of Black Thor showing similar textures. Sample 1331691, DDH FN-09-01, 152.15 m. Py—pyrite; Po—pyrrhotite; Ccp—chalcopyrite.

iron-formations below the Black Thor Intrusive Complex (Fig. 3B), consistent with them being the source of the oxide in this deposit.

There are examples where magmas have thermomechanically eroded oxide-facies iron formation (e.g., Duluth [Minnesota, USA]: Ripley, 1986; Digger's Rock [Western Australia]: Perring et al., 1996; Hunters Road [Zimbabwe]: Prendergast, 2003); however, none of these systems contain anomalous chromite. In the case of Duluth, the magma may have been too poor in Cr, whereas the magma at Digger's Rock and Hunters Road may have been undersaturated in chromite. Unfortunately, none of these studies reported the Cr contents of the oxide xenoliths. The country rocks of the Sukinda and the Inyala intrusions include iron formation, but no iron-formation xenoliths were reported by Chakraborty and Chakraborty (1984), Mondal et al. (2006), or Rollinson (1997). The Kemi intrusion contains Na-rich gneissic xenoliths; however, no iron-formation xenoliths were reported by Alapieti et al. (1989).

There are <2-cm-thick chromite layers in strongly differentiated komatiite flows where chromite has reached saturation after significant degrees of fractional crystallization (e.g., Kambalda: Lesher, 1989) and rare occurrences of Cr-rich lavas (e.g., Halkoaho et al., 2000), but the amount of chromite is very small and it is clear that it formed via fractional crystallization. The absence of thick chromite seams in komatiitic, picritic, or basaltic lavas suggest that despite its fine grain size and theoretical high transportability (see Lesher, 2017), chromite is normally trapped at the same stratigraphic levels where it forms and is not normally transported significant distances vertically, likely because it forms larger untransportable "pseudoslugs".

The proposed process (Fig. 4) requires further testing; however, it explains a major paradox in the genesis of conduit-hosted, if not all, stratiform chromite deposits. It may also have applications in the genesis of some intrusions containing anomalous amounts of Fe-Ti-V oxides associated with high-Ti, low-Cr basaltic magmas.

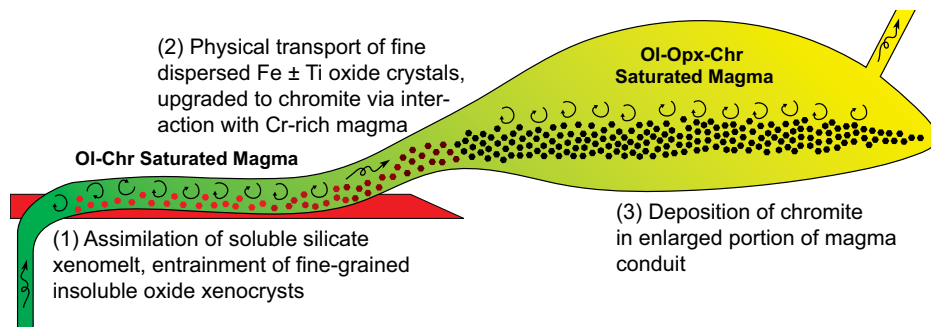


Figure 4. Model for dynamic upgrading of Fe ± Ti oxides derived from oxide-facies iron formation or ferrogabbro via interaction with Cr-rich komatiitic magma. OI—olivine; Chr—chromite; Opx—orthopyroxene.

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