Parental magma composition of the Main Zone of the Bushveld Complex: Evidence from in-situ LA-ICP-MS trace element analysis of silicate minerals in the cumulate rocks

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ABSTRACT:

In-situ trace element analysis of cumulus minerals may provide a clue to the parental magma from which the minerals crystallized. However, this is hampered by effects of the trapped liquid shift (TLS). In the Main Zone (MZ) of the Bushveld Complex, the Ti content in plagioclase grains shows a clear increase from core to rim, whereas most other elements (e.g., rare earth elements (REEs), Zr, Hf, Pb) do not. This is different from the prominent intra-grain variation of all trace elements in silicate minerals in mafic dikes, which have a faster cooling rate. We suggest that crystal fractionation of trapped liquid occurred in the MZ of Bushveld and the TLS may have modified the original composition of the cumulus minerals for most trace elements except Ti during slow cooling. Quantitative model calculations suggest that the influence of the

TLS depends on the bulk partition coefficient of the element. The effect on highly incompatible elements is clearly more prominent than on moderately incompatible and compatible elements because of different concentration gradients between cores and rims of cumulate minerals. This is supported by the following observations in the MZ of Bushveld: 1) positive correlation between Cr, Ni and Mg# of clinopyroxene and orthopyroxene, 2) negative correlation between moderately incompatible elements (e.g., Mn and Sc in clinopyroxene and orthopyroxene, Sr, Ba, Eu in plagioclase), but 3) poor correlation between highly incompatible elements and Mg# of clinopyroxene and orthopyroxene or An# of plagioclase. Modeling suggests that the extent of the TLS for a trace element is also dependent on the initial fraction of the primary trapped liquid, with strong TLS occurring if the primary trapped liquid fraction is high. This is supported by the positive correlation between highly incompatible trace element abundances in cumulus minerals and whole-rock Zr contents.

We have calculated the composition of the parental magma of the MZ of the Bushveld Complex. The compatible and moderately incompatible element contents of the calculated parental liquid are generally similar to those of the B3 marginal rocks, but different from the B1 and B2 marginal rocks. For the highly incompatible elements, we suggest that the use of sample with the lowest whole-rock Zr content and the least degree of TLS is the best approach to obtain the parental magma composition. The HREE contents of the magma calculated from orthopyroxene are similar to B3 rocks and lower than B2 rocks. The calculated REE contents from clinopyroxene are generally significantly higher than B2 or B3 rocks, and that from plagioclase are in the lower level of B2 but slightly higher than B3. However, the calculated REE patterns from both clinopyroxene and plagioclase show strong negative Eu anomalies, which are at the lower level of B2 field and within the B3 field, respectively. We suggest that Eu may be less affected by TLS than other REEs due to its higher bulk compatibility. Based on this and the fact that the calculated REE contents of the parental magma should be higher than the real magma composition due to some degree of crystal fractionation and TLS even for the sample with the lowest amount of trapped liquid, we propose that a B3 type liquid is the most likely parental magma to the MZ of the Bushveld Complex. In the lowermost part of the MZ, there is involvement of the Upper Critical Zone (UCZ) magma.

KEYWORDS: Parental magma, in-situ trace element analysis, LA-ICP-MS, B1, B2 and B3 marginal rocks, Main Zone, Bushveld Complex

INTRODUCTION

There have been different approaches to constrain the composition of the parental liquid(s) to mafic layered intrusions. In many studies, the crystallization history of the cumulate rocks have been modeled based on fine-grained contact rocks or dikes and sills spatially associated with the intrusion (Cawthorn *et al.*, 1981; Sharpe, 1981; Davies & Tredoux, 1985; Harmer & Sharpe, 1985; Sharpe & Hulbert, 1985; Curl, 2001; Cawthorn, 2006; Namur *et al.*, 2010; Barnes *et al.*, 2010; Seat *et al.*, 2011; Godel *et al.*, 2011b), but the contact rocks are often contaminated. One way to estimate the bulk magma is to calculate the weighted average composition of the cumulate rocks (e.g., Morse, 1981; VanTongeren et al., 2010), but this requires comprehensive sampling and may lead to imprecise results for intrusions that have behaved as an open system. Whole-rock mass balance is used to estimate the parental magma composition of trace elements assuming that the whole-rock trace element content represents the sum of the concentrations of an element in the cumulus fraction and trapped liquid, with the latter assumed to represent the melt composition (Cawthorn, 1991; Bédard 2001; Godel *et al.*, 2011a). However, the initial proportion of trapped liquid is difficult to estimate if post-cumulus overgrowth has taken place (Godel *et al.*, 2011a). The fourth method, in-situ trace element analysis of silicate minerals coupled with mineral/melt partition coefficients, could potentially be used to calculate the trace element composition of magma (Bédard, 1994, 2001; Eales, 2000; Godel *et al.*, 2011a; VanTongeren & Mathez, 2013). However, the trace element abundances of the cumulus minerals may have been modified by effects of the trapped liquid shift (TLS) (Barnes, 1986; Mathez, 1995; Pun *et al.*, 1997; Wilson *et al.*, 1999; Godel *et al.*, 2011a; Tanner *et al.*, 2014; Chen et al., 2017) or by inter-mineral diffusion (Tanner *et al.*, 2014), hampering the use of in-situ trace element analyses for obtaining the original compositional information on cumulus minerals. Yet, it is not well constrained how the concentrations of different trace elements are modified.

Much attention has been paid to unravelling the composition of the parental magmas to the Bushveld Complex in South Africa, the world's largest layered intrusion containing more than 70% of the world's platinum-group element (PGE) resources (Vermaak, 1995; Cawthorn, 1999) and a considerable proportion of the global V and Cr resources (Polyak, 2010). Three types of marginal rocks, designated as Bushveld 1–3 (B1–B3), are believed to be representative of magmas that formed of the Bushveld Complex (Sharpe, 1981; Harmer & Sharpe, 1985; Sharpe & Hulbert, 1985). The B1 rocks are chemically magnesian andesites and spatially related to the Lower Zone (LZ) and Lower Critical Zone (LCZ), while the B2 and B3 rocks are tholeiitic in composition and underlie the Upper Critical Zone (UCZ) and Main Zone (MZ), respectively. The B1 marginal rocks contain mainly orthopyroxene and minor olivine, and the B2 and B3 rocks are composed mainly of plagioclase, orthopyroxene, and clinopyroxene (Barnes *et al.*, 2010). The B1 marginal rocks have been dated at 2050 ± 6 Ma, and a B2 rock has given an age of 2052 ± 6 Ma (Curl, 2001), being similar to the ages of 2056.88 ± 0.41 Ma and 2057.04 ± 0.55 Ma determined for the Merensky Reef in Western and Eastern Bushveld, respectively (Scoates & Wall, 2015). Based on geochemistry, it has been proposed that the LZ and LCZ were derived from a B1-type magma (Barnes et al., 2010; Godel et al., 2011a).

The composition of the parental magma to the Main Zone cumulates remains less well constrained. Harmer & Sharpe (1985) suggested that the MZ was generated from a B3 magma based on the occurrence of B3 marginal rocks adjacent to that zone. Maier & Barnes (1998) also suggested that the MZ was derived from B3-type melts, based on similar whole-rock REE patterns of the MZ cumulates and the B3 marginal sills. Based on whole-rock mass balance, Cawthorn et al. (1991) concluded that the feeding magma at the Pyroxenite Marker on the top of MZ was more akin to the B2 marginal rocks. However, the calculated parental magma generally has higher incompatible trace element abundances than B2 rocks. VanTongeren & Mathez (2013) reached a similar conclusion using trace element contents of cumulus minerals and mineral/melt partition coefficients assuming that the cores of cumulus minerals have preserved their original trace element abundances. However, the effects of TLS on trace element contents may not be restricted to the rims of cumulus mineral but the cores may also have been modified (Pun et al., 1997; Godel *et al.*, 2011a; Tanner *et al.*, 2014).

In this study, we determined in-situ trace element compositions of cumulus minerals from the Main Zone of the Bushveld Complex. Our aims were: 1) to evaluate the controlling factors on the distribution of trace elements in cumulus minerals and 2) to constrain the parental magma composition of the MZ.

GEOLOGICAL BACKGROUND

The Bushveld Igneous Complex in central Transvaal is exposed as the western, eastern and northern lobes, covering an area of about 40,000 km^2 (Cawthorn, 2015). Despite the huge size of the intrusion, recent high-precision age determinations have provided evidence for a short time period of emplacement and cooling of the whole ultramafic-mafic cumulate sequence (the Rustenburg Layered Suite) within approximately one million years at 2.056

Ga (Zeh *et al.*, 2015, Mungall *et al.*, 2016). The stratigraphic succession, which attains a maximum thickness of 8 km, is subdivided into five major zones (South African Committee for Stratigraphy, 1980) as shown in Fig. 1. A detailed description of the different zones is available in Maier *et al.* (2013) and references therein and only some basic features of the MZ are summarized here. Based on the variation in mineral modes and compositions, Mitchell (1990) subdivided the MZ below the Pyroxenite Marker into six units, two relatively thin norite units at the bottom, which are overlain by four thicker gabbronorite units (Fig. 2). Some weak mineral compositional reversals are interpreted as results of small magma replenishments (Fig. 2; Mitchell, 1990). Near the base of the Pyroxenite Marker, which defines the upper boundary of the MZ, a persistent reversal in mineral compositions and decrease in whole-rock Sr isotope ratios are recorded, indicating a large magma replenishment (Sharpe, 1985; Cawthorn *et al.*, 1991; Tenger *et al.*, 2006; VanTongeren & Mathez, 2013; Tanner *et al.*, 2014). Intervals that show distinct centimeter- to meter-scale layering are largely confined to the upper part of the MZ near the Pyroxenite Marker and underlying rocks (Quadling & Cawthorn, 1994).

In the lower part of the MZ there are pyroxenite layers with euhedral orthopyroxene occurring as the sole cumulus mineral and interstitial clinopyroxene and plagioclase (sample A297, Figs. 3a, b). Most of the MZ rocks show a granular texture, with subhedral crystals of clinopyroxene and orthopyroxene occurring between plagioclase laths (Fig. 3c). The rocks typically contain 10–30 vol% orthopyroxene, 20–30 vol% clinopyroxene, and 40–70 vol% plagioclase (Fig. 3c). The low-Ca pyroxene is dominated by orthopyroxene, but pigeonite occurs near the Pyroxenite Marker in the upper part of the MZ (Fig. 3d). In some cases, plagioclase grains are partly or entirely enclosed in orthopyroxene, but rarely in clinopyroxene (Fig. 3e). The enclosed plagioclase grains generally show a rounded shape and are smaller than other unenclosed grains (Mitchell, 1990). In rare occurrences in the northern limb, clinopyroxene has been reported to enclose orthopyroxene, which in turn enclose grains of plagioclase (Roelofse *et al.*, 2012), suggesting a crystallization sequence of plagioclase-orthopyroxene- clinopyroxene. In many samples, biotite occurs at the boundary of pyroxene and plagioclase grains (Fig. 3f).

Sampling and whole-rock geochemistry

Samples of this study were taken from drill cores labeled as SK-2 in the mining lease area of Rustenburg Platinum Mines, Union Section, in the northern sector of the western Bushveld Complex (Fig. 1). The samples span a stratigraphic height from 4000 to 2300 m above the base of the complex and cover almost the whole section of the MZ (Fig. 2). Whole-rock compositions of the samples were determined by Maier *et al.* (2013) and are listed in Table 1. In Fig. 4, primitive mantle-normalized trace element compositions of the studied cumulate samples are compared with those of B2 and B3 marginal rocks, which are potentially similar in chemical composition to the parental magma of the MZ rocks.

Sample A65 has the lowest whole-rock Zr content, and no biotite was identified under microscope, whereas sample A106 with the highest whole-rock Zr content shows a biotite content of ~5% (Figs. 3f, g). Sample A238 is distinguished from other samples by the presence of iron oxide minerals with clearly higher Mn and V contents. (Figs. 3h, 4).

METHODS

Major element compositions of the silicate minerals, including orthopyroxene, clinopyroxene, and plagioclase, were determined at Laval University (Quebec City, Canada) using a Cameca SX100 electron microprobe. The microprobe was operated in wavelength dispersive mode (WDS) using an acceleration voltage of 15 kV, a beam current of 20 nA, a beam diameter of 2–5 μm, and counting times set to 20 and 10 s on the peaks and backgrounds, respectively (Godel *et al.*, 2011a).

Trace element concentrations of the minerals of 6 samples were analyzed by laser-ablation inductively coupled mass spectrometry (LA-ICP-MS) at the LabMater Laboratory in the University of Quebec at Chicoutimi (UQAC) using a Thermo X7 mass spectrometer coupled with a New Wave Research 213 nm Nd: YAG UV laser ablation system. The analyses were conducted using 80 μm diameter spots, a laser frequency of 10 Hz, a power of 0.8 mJ/pulse, and He–Ar carrier gas. The gas background was collected for 20 s followed by 60 s of data acquisition. The ablated material was analyzed by ICP-MS operated in time-resolved mode using peak jumping. NIST-610 reference material was used for calibration and NIST-612 as a monitor (Godel *et al.*, 2011b). The results of NIST-612 and detection limits are listed in online Supplementary Data. The reduction of the data was computed using Plasma Lab software (Thermo Elemental) and ^{29}Si as an internal standard (Godel *et al.*, 2011a). Trace element concentrations of the minerals of 10 samples (6 have previously been analyzed in Quebec) were analyzed at the Geological Survey of Finland (GTK) in Espoo using an AttoM Single Collector High Resolution ICP-MS, coupled with Photon MachinesTM deep UV (193 nm wavelength) excimer laser system. The analyses were conducted using 50 μm diameter spots, a laser frequency of 10 Hz, a power of 4.68J/cm^2, and He-Ar carrier gas. The gas background was collected for 20 s followed by 60 s of data acquisition. BHVO-2G reference material was used for calibration and BCR-2G as a monitor. The reduction of the data was computed using Glitter software and ^{29}Si as an internal standard. The results of BCR-2G and detection limits are listed in online Supplementary Data.

ANALYTICAL RESULTS

All data of spot analyses of orthopyroxene, clinopyroxene and plagioclase are listed in Supplementary Data. The average values of several spots of the three minerals are listed in Tables 2, 3, 4. The Mg# values [atomic 100*Mg/(Mg+Fe)] of Opx and Cpx and the An# values [atomic 100*Ca/(Ca+Na)] of plagioclase are based on microprobe data and all trace element compositions on LA-ICP-MS analyses. The trace element concentrations obtained for the standards deviate less than 5-10% from the recommended values both in the Quebec and Espoo analyses. As the calibration standard BHVO-2G may be better than NIST-610 (Liu et al., 2010), we only use the trace element data obtained in Espoo for most of our discussion. However, the comparison analyses between core and rim (not traverse analyses) determined in Quebec is also used for discussion because the compositional comparison between core and rim of mineral grains may have not been affected by calibration standard at all.

Orthopyroxene

The Mg# values of orthopyroxene range from 56.9 to 75.5. In general, Mg# decreases upwards in the stratigraphy, excluding sample A238, and are consistent with the results of Mitchell *et al.* (1998) (Fig. 2). The analyzed orthopyroxene grains from the MZ have Cr contents in the range of 10–713 ppm and the Ni contents vary from 224 to 681 ppm. They have considerable amounts of some other minor elements: Mn from 2600 to 4400 ppm, Sc from 34 to 47 ppm, and Co from 123 to 184 ppm. Of the three major silicate minerals (orthopyroxene, clinopyroxene, plagioclase), orthopyroxene has the lowest concentrations for most incompatible trace elements and are characterized by relatively low LREE abundances compared to HREE, which is consistent with the experimentally determined orthopyroxene/melt partition coefficients for these elements (e.g., Bédard, 2001 and references therein) (Fig. 5). On the primitive mantle-normalized multi-element plot presented in Fig. 5a, all orthopyroxene compositions are depleted in Ba, Sr, Eu, but not in Zr and Hf, and slightly enriched in U and Ti. Niobium was not plotted because its abundance is close to the detection limit.

Clinopyroxene

The Mg# values in clinopyroxene range from 65.1 to 83.6 and correlate well with Mg# of orthopyroxene in the same sample (Fig. 2). The Cr, Ni, Mn and Sc contents in clinopyroxene also exhibit positive correlation with the abundances in orthopyroxene (not shown). Clinopyroxene contains considerable amounts of both LREE and HREE. Primitive mantle-normalized trace element patterns are almost flat for REE, with LREE (e.g., Ce) occurring at 2–10 times and HREE (e.g., Yb) at 3–7 times of the mantle abundances (Fig. 5b). There are negative Sr, Eu and Ti anomalies compared to the neighboring REEs (Fig. 5b).

Plagioclase

The An# values of plagioclase range from 58.2 to 71.2 (Fig. 2). On the primitive mantle-normalized trace element diagram of Fig. 5c, plagioclase is enriched in Ba, Sr, and Eu, consistent with the relatively high plagioclase/melt partition coefficients of these elements (e.g., Bédard, 2001). The analyzed plagioclase crystals have relatively high LREE contents and very low Cr, U, Y, Zr, Hf and HREE contents (Fig. 5c; U, Zr and Hf not shown).

Compositional variation across stratigraphy

Excluding sample A238, Mg# of clinopyroxene and orthopyroxene show a positive correlation and exhibit a general decreasing trend upwards (Fig. 2). However, the An content of plagioclase does not correlate well with Mg# of pyroxenes (Fig. 2), similarly to the observations of Mitchell et al. (1990) and Roelofse & Ashwal (2012). Sample A238 shows an offset from the main fractionation trend from the bottom to the top with clearly lower Mg# in both clinopyroxene and orthopyroxene (Fig. 2). For both orthopyroxene and clinopyroxene, Cr and Ni exhibit a similar variation to that of Mg# (excluding samples A238 and A297), while a negative correlation with Mg# can be observed for Mn and Sc. No systematic correlation is present between Mg# and other trace elements (e.g., REEs, Zr). In the case of plagioclase, Sr, Ba, and Eu have rough opposite variation trends across stratigraphy compared with An# (excluding sample A238 and A297), while other trace elements (e.g., LREE) show no clear correlation(Figs. 6, 7, 8).

Intra-grain and inter-grain variation

Orthopyroxene has a very low intra-grain variation in Mg# (Fig. 9a), Cr (Fig. 9b), Ni, Mn, Sc, or HREE (Yb shown in Fig. 9c) whereas the intra-grain variation in Ti is more evident (Fig. 9d). Clinopyroxene shows a slightly higher intra-grain variation in Mg# than orthopyroxene (Fig. 10a). The intra-grain variations of Cr (Fig. 10b), Ni, Mn and Sc are not significant, which is also true for REE and Zr (Ce shown in Fig. 10c), but that of Ti is clear (Fig. 10d). Plagioclase shows a higher intra-grain variation in An# than orthopyroxene and clinopyroxene in Mg# (Fig. 11a). There are no core-rim differences in the Sr, Ba or Eu contents of plagioclase (Sr shown in Fig. 11b). Neither LREE (Ce shown in Fig. 11c) nor Zr show prominent variations. It is worth noting that the intra-grain variation of Ti is more conspicuous than that of other elements and that the variation of Ti in plagioclase is more scattered than in orthopyroxene and clinopyroxene.

To better understand the mechanism of intra-grain chemical variation, we have conducted rim-to-core or rim-to-core-to-rim traverse analyses of plagioclase grains from two samples with different whole-rock Zr contents (Tables, 5, 6; Fig. 12). For most plagioclase grains, the outermost rim shows a sharp increase in An# coupled with a sharp decrease in Ti (Fig. 12). However, excluding the outermost rim, there is a clear progressive outward decrease in An# coupled with an increase in Ti, with about 20-50% higher in cores than that of rims. In contrast, there is much lower core-to-rim variation for LREEs (Ce shown) (Figs. 12a, b, c, d). For a couple of grains, the rim has about 15% higher Ce than the core, but for most grains the elevation of Ce from core to rim is less than 10%. For Sr, Ba and Pb, there is almost no core-rim variation. For a couple of grains, there is complex variation of An# from core to rim, and it is worth noting that the Ti contents always show negative correlation with An# but the other trace elements (LREEs, Sr, Ba, Pb) do not show much variation (Figs. 12e, f).

The samples generally show a low inter-grain variation of less than 2 times of the within-sample variation (Figs. 6, 7, 8). As in the case of the intra-grain variation, Ti shows a higher inter-grain variation in each sample compared to other elements for the three minerals, with the one sigma standard deviation being ~15% for Ti and ~5% for other elements (Fig. 8).

Correlation between element contents and degree of crystal fractionation

The bulk-rock partition coefficient D of an element is dependent on the partition coefficients of the element for different minerals and the proportions of these minerals during crystallization. The partition coefficients of elements for different minerals used in this work are from the compilation of Bédard (2001), and the bulk partition coefficients are estimated assuming that the modal percentages of plagioclase, orthopyroxene and clinopyroxene are 50%, 25%, and 25%, respectively, based on our CIPW calculations (Table 7) and Mitchell (1990) (Fig. 2). Chrome and Ni are compatible in both clinopyroxene and orthopyroxene, and their calculated bulk partition coefficients in the Bushveld MZ are slightly higher than 1 (D=1.2). Manganese, Sc, and Zn are compatible in orthopyroxene and clinopyroxene, but highly incompatible in plagioclase. Due to the high abundance of plagioclase, the bulk partition coefficients of these elements are lower than 1 (D = 0.5) and thus the elements are moderately incompatible. Strontium is compatible in plagioclase, whereas Ba and Eu are moderately incompatible in plagioclase, with their bulk partition coefficients falling slightly below 1 (D = 0.5 to 0.8). For REEs, Zr, Hf, and Ti, the bulk D values range from 0.1 to 0.2 and for Nb, D is <0.01, making these elements highly incompatible.

To assess whether these elements behave systematically, we plotted different elements in pyroxenes against their Mg# and those in plagioclase against An# using our data from the Western Bushveld MZ coupled with data from the Eastern Bushveld MZ and Northern Bushveld MZ published by VanTongeren & Mathez (2013) and Tanner *et al.* (2014), respectively (Figs. 13, 14, 15). Available data from the UZ of Eastern and Northern Bushveld is also plotted (VanTongeren & Mathez, 2013; Tanner *et al.*, 2014). There is generally a positive correlation between Mg# and the compatible elements contents of both orthopyroxene and clinopyroxene (e.g., Cr, Ni; Figs. 13, 14). For moderately incompatible elements, a broadly negative correlation with respect to Mg# or An# is observed (e.g., Mn, Sc, Sr, Ba, Eu; Figs. 13, 14, 15). On the Ni vs. Mg# and Sc vs. Mg# diagrams of clinopyroxene, two samples from the MZ of Eastern Bushveld plot away from the main trend, but they are anorthosites (Figs. 14b, d). Samples from the UZ broadly plot on the same trend as the MZ samples. However, for highly incompatible elements, there is much poorer correlation with Mg# or An#.

Correlation with whole-rock Zr contents

As Zr is highly incompatible and could be used as an index of the amount of trapped liquid (e.g., Wilson et al., 1999; Cawthorn, 2015), trace element contents of minerals are plotted against whole-rock Zr contents in Figs. 16–18. The Zr content of one of the samples (A238) from Western Bushveld probably contains inherited zircon and therefore its Zr content is corrected utilizing the positive correlation between Nb and Zr, with the method being described in Supplementary Data. Available UZ samples published from Eastern Bushveld by VanTongeren (2011) and VanTongeren & Mathez (2013) are also included. There is generally a positive correlation between whole-rock Zr and highly incompatible elements in clinopyroxene and plagioclase of MZ samples (e.g., REEs and Zr in clinopyroxene, LREEs in plagioclase). The UZ samples from Eastern Bushveld plot on the same trend with the MZ samples of Western Bushveld. However, such correlations are not present for orthopyroxene. On the other hand, moderately incompatible elements show poor correlation with whole-rock Zr (e.g., Sc in Cpx and Opx, Figs. 16, 17; Sr, Eu, Ba in Plag, Fig. 18). The compatible elements (Cr, Ni in orthopyroxene and clinopyroxene) neither have any correlation with whole-rock Zr (not shown).

The lower portion of the MZ

Sample A297, the stratigraphically lowest one among our samples (height 2296 m), is located near the bottom of the MZ. In this sample, orthopyroxene occurs as clearly euhedral crystals, whereas both clinopyroxene and plagioclase grains show anhedral interstitial textures. Both orthopyroxene and clinopyroxene have high Mg# (76, 84; the highest among the analyzed samples), slightly higher than in the overlying sample A271 (height 2436 m), whereas placioclase grains show relatively low An# (Fig. 2). This sample also yielded the highest compatible element contents (e.g., Cr and Ni). On the other hand, the sample has clearly much higher incompatible trace element contents in silicate minerals than other samples (Figs. 6, 7, 8). The plagioclase grains have clearly higher LREE, with the enrichment relative to the overlying samples ranging from ~3 times for La to ~2 times for Ce, Pr, Nd and ~1.5 times for Sm and Eu. However, they have slightly lower or comparable Sr and Ba contents (Fig. 8). A similar trend is observed for clinopyroxene, with the enrichment relative to other samples decreasing from LREE to HREE, but the enrichment in Sc, Ti, V is absent. For orthopyroxene, there is a small enrichment in MREE but that of HREE is not clear (Figs. 6, 7, 8).

DISCUSSION

Fractional crystallization

Mitchell *et al.* (1990) carried out a systematic study of the mineralogy and mineral compositions of the MZ of Western Bushveld. Based on the progressive upwards decreasing Mg# of orthopyroxene with minor compositional reversals, the authors concluded that the MZ below the Pyroxene Marker in Western Bushveld is dominated by crystal fractionation with minor magma replenishments (Fig. 2). Our new compositional data on orthopyroxene (e.g., Mg#) are broadly consistent with the variation trend of Mg# presented by Mitchell *et al.* (1990). Crystal fractionation is also supported by the variation of Mg# in clinopyroxene, compatible elements (e.g., Cr, Ni in both orthopyroxene and clinopyroxene), moderately incompatible elements (e.g., Mn, Sc of both clinopyroxene and orthoypyroxene, and Sr, Ba, Eu of plagioclase). However, highly incompatible elements (e.g., REEs, Zr) in the three minerals show decoupling from Mg# in orthopyroxene or An# in plagioclase (Fig. 6, 7, 8).

In addition to normal fractional crystallization processes, reactive melt flow is considered to be an important process in mafic magma chambers both in the oceanic lower crust (Coogan *et al.*, 2000; Lissenberg & Dick, 2008; Lissenberg *et al.*, 2013; Sanfilippo *et al.*, 2015) and in mafic layered intrusions (Irvine, 1980; Methaz *et al.*, 1995; Holness *et al.*, 2007; Namur *et al.*, 2013). In such a process, hot infiltrating fluid could potentially dissolve minerals in a crystal mush and precipitate new minerals, which can potentially explain the decoupling of highly incompatible elements from compatible elements in the MZ of Bushveld. However, in the MZ of the Bushveld Complex, one striking feature is the limited intra- and inter-grain-scale variation of incompatible trace elements in silicate minerals (less than 2 times) (Figs. 6, 7, 8). This is also consistent with the low variation of more-to-less incompatible element ratios. These features indicate that reactive melt flow may be not have been active in the MZ of Bushveld.

Evolution of trapped liquid and diffusive modification

The crystallization of trapped interstitial liquid depends on the mobility of the liquid and the permeability of the crystal mush. Adcumulus-style crystallization occurs if there is a high permeability of the crystal mush, allowing evolving intercumulus liquid to maintain communication with the liquid in the main magma reservoir by diffusion and/or convection, and if compaction, annealing, and grain boundary re-adjustment take place (e.g., McKenzie, 1984; Kerr & Tait, 1986; Tait & Jaupart, 1992; Tegner et al., 2009). On the other hand, orthocumulus-style crystallization will operate if the circulation of the interstitial liquid is not efficient, involving overgrowth of primocrysts and evolved interstitial phases that crystallized from the trapped liquid. The Bushveld MZ rocks more likely crystallized as an orthocumulate system with considerable interstitial liquid fractionation, which is reflected by overgrowth textures of cumulus minerals (Mitchell *et al.*, 1990; this study). In such a system, core-to-rim variation of An# in plagioclase would be expected, as An# of plagioclase is considered resistant to diffusive modification under magmatic conditions due to the slow charge-coupled substitution of CaAl with NaSi (Grove *et al.*, 1984; Morse, 1984, 2008; Cherniak, 2003; Tegner & Cawthorn, 2010). Also, zonation of incompatible trace elements in cumulus minerals would be present as these elements tend to increase during the fractionation of trapped liquid in a relatively closed system (Humphreys *et al.*, 2009; Godel *et al.*, 2011a). Because of its slow diffusion, Ti in plagioclase is a good parameter for recording the evolution of interstitial liquid (Humphreys *et al.*, 2009). In the Bushveld MZ, there is an up to two-fold intra-grain scale difference in the Ti content of plagioclase grains. Some grains show a higher Ti content in the rim than in the core, fitting well with a process of trapped liquid crystallization (Fig. 11). However, some plagioclase rims show a lower Ti content than the corresponding cores. In the Skaergaard intrusion, the decreasing trend of Ti in plagioclase towards the rim has been interpreted to reflect the onset of magnetite crystallization in the trapped liquid, which occurred when the An# value of plagioclase decreased down to about 55 (Humphreys *et al.*, 2009). This is not applicable to our samples because of the scarcity of magnetite.

Traverse analyses of plagioclase grains further show that many grains have a sharp increase of An coupled with a sharp decrease of Ti in the outermost rim of plagioclase grains (Fig. 12). This cannot be explained by percolation of interstitial melt as this melt is normally is rather evolved and should produce a lower An# value and higher Ti content in plagioclase. Nevertheless, it explains why some rims show lower Ti than cores (Fig. 11). However, if not considering the outmost part of plagioclase grains, a clear outward decrease in An# coupled with an increase in Ti is observed for many plagioclase grains, providing robust evidence for crystallization of trapped interstitial liquid (Fig. 12a, b, c, d). Zonation of Ti has been reported both in orthopyroxene and clinopyroxene from the LZ and LCZ of the Bushveld Complex (Godel et al., 2011a) and the Mont de Crystal intrusion (Maier et al., 2015), which is interpreted as closed-system crystallization of the trapped liquid with progressively enriched incompatible element contents in the liquid. For a few grains, the complex zonation of An# from core to rim may reflect re-adjustment of crystal boundaries (Boudreau, 1999), however, the negative correlation between An# and Ti indicates overgrowth of plagioclase from trapped liquid also occurred for these grains (Figs. 12e, f).

Because the bulk-rock partition coefficients of other elements (e.g., REE, Pb) are comparable to that of Ti, the element enrichments in the evolving trapped liquid should be at a similar level. However, traverse analyses of plagioclase grains of these elements show much lower core-to-rim variation, which is clearly different from the behavior of Ti (Fig. 12). This is consistent with the small intra-grain-scale variation of REEs in plagioclase revealed by core-rim associations, which is clearly much lower than that of Ti (Fig, 11). In addition, the inter-grain variation of REE within the thin-section scale is clearly lower than that of Ti, with a relative standard derivation of about 5% (1σ) for REEs and about 15% (1σ) for Ti (Fig. 8). The contrasting behavior of REEs and Ti in the Bushveld MZ samples provides a strong argument that the diffusion rate of REEs in plagioclase is faster than that of Ti. Experimental studies suggest that the diffusion rate of an element in plagioclase is highly dependent on the charge of the cation, with the univalent cations diffusing faster than the divalent cations and the latter in turn faster than the trivalent cations (Charniak, 2003). Though there are no direct experiment data for diffusion of Ti, as a quadrivalent cation, it likely diffuses slower than the trivalent REEs (Charniak, 2003). In contrast, in the ~2.44 Ga mafic dikes in the Fennoscandia Shield, 2- to 3-fold core-to-rim enrichment in REEs and Ti has been observed in clinopyroxene grains (our unpublished data). A core-to-rim variation of REE has also been reported in clinopyroxene of the Rum intrusion (Leuthold *et al.*, 2014). Because the cooling rate in mafic dike and small intrusion (e.g., Rum) is faster than that in large intrusions like Bushveld, we suggest that the chemical zonation produced by closed-system crystal fractionation in the former is generally quenched due to fast cooling, whereas the concentration gradients between core and rim may have been erased in Bushveld by diffusion of REEs.

Quantitative modeling of the final trapped liquid composition

During the solidification of mafic crystal mushes, the crystal framework is thought to contain 40–70% of trapped liquid (e.g., Shirley, 1986; Philpotts & Carroll, 1996; Philpotts *et al.*, 1998; Jerram *et al.*, 1996, 2003; Donev *et al.*, 2004). We assume a two-stage process in which the overgrowth of crystals is faster than the element diffusion: 1) During closed-system fractionation of trapped liquid with overgrowth of cumulus minerals, the incompatible elements tend to increase in the evolving trapped liquid, resulting in increasing element contents in the rim, which is similar to the observed enrichment trend in mafic dikes; 2) Due to the chemical potential gradient between the core and rim in cumulus minerals, there could be subsequent diffusion of these elements (Godel *et al.*, 2011a, Tanner *et al.*, 2014).

The final abundance of plagioclase, orthopyroxene and clinopyroxene in cumulate rocks has been calculated on the basis CIPW norms of whole-rock compositions (Table 5, data from Maier *et al.*, 2013). The minor phases,such as K-feldspar, quartz, magnetite, ilmenite, apatite, and biotite, with a total abundance of about 4 wt% are thought to represent the solidification of final-stage trapped liquid (Table 5). The evolving liquid composition is modeled using the following Rayleigh fractionation equation:

$C_{Liq} = C_0F^{(D-1)}$

in which C_0 and C_{Liq} are the element contents in the primary trapped liquid and the evolving trapped liquid, respectively, and F is the initial fraction of the trapped liquid. The partition coefficients of elements in different minerals are from Bédard (2001). The bulk partition coefficients D are estimated assuming the approximate mineral fractions of plagioclase, orthopyroxene and clinopyroxene to be 0.5, 0.25, and 0.25, respectively, based on the calculated CIPW norms (Table 5).

We use C_{Liq}/C_0 to reflect the compositional change between the fractionating trapped liquid and the primary trapped liquid. The fraction of primary trapped liquid is assumed to be from 20 to 40%.The C_{Liq}/C_0 ratio is calculated to be the following for elements with different bulk partition coefficients: 1) about 0.3 to 0.6 for compatible elements with D from 1.5 to 1.2; 2) 1.6 to 3.2 for moderately incompatible elements with D from 0.8 to 0.5; 3) 6.3 to 7.9 for incompatible elements with D from 0.2 to 0.1 (Fig. 19), and 4) about 10 for highly incompatible elements with D of about 0.01 (not shown). It is clearly that the enrichment of elements in the fractionated trapped liquid is negatively correlated with the bulk partition coefficients, with the highest enrichment for the most incompatible elements.

Modeling the degree of trapped liquid shift

Because of the absence of zonation of REE in cumulus minerals, we assume that the cores and progressively enriched rims in the three minerals have equilibrated and the final element contents in the mineral grains after TLS will be the average content of the cumulus core and overgrown rim. In the following, we calculate the degree of enrichment in the final cumulus minerals based on the following mass balance:

$$C_{Rim} = (\int C_{Liq} \times D \, dF_{Rim})/F_{Rim} \qquad (2)$$

$$C_{Final} = (C_{Rim} \times F_{Rim} + C_{Core} \times F_{Core}) / (F_{Rim} + F_{Core}) \qquad (3)$$

$$\text{Trapped liquid shift (TLS) (\%)} = (C_{Final} - C_{Core})/ C_{Core} \times 100 \qquad (4)$$

F_{Rim} is the fraction of overgrown rim and dF_{Rim} is differential calculus of overgrown rim. D is bulk partition coefficient. C_{Core} and C_{Rim} are the element contents in the primary core and overgrown rim with changing composition, respectively, and C_{Final} is the final content after core-rim homogenization. The calculated results show that the REE contents in cumulus minerals after TLS will be about 25 to 35% higher than the primary core compositions for elements with bulk partition coefficients of 0.2 to 0.1, respectively, if we assume that the primary trapped liquid fraction was 30%. For moderately incompatible elements with bulk partition coefficients from 0.8 to 0.5, the bulk cumulate contents will be enriched by 4–13%. For compatible elements, such as Cr and Ni, the final concentrations in clinopyroxene and orthopyroxene could be about 1 to 7% lower than the original contents, assuming a bulk partition coefficient of 1.2. From the calculation presented above, the concentrations in the final cumulus minerals have been modified variably by TLS, depending on the bulk partition coefficient, with the TLS of incompatible elements being clearly more intensive than that of moderately incompatible elements and compatible elements.

Another potential contribution to the variation of the TLS would be the primary amount of trapped liquid (Barnes *et al.*, 1986; Arndt *et al.*, 2005; Cawthorn *et al.*, 2015). For incompatible elements, the concentrations in the final trapped liquid (4 wt%) would be enriched by 4 to 8 times (D=0.1), assuming an original trapped liquid fraction in the range of 20–40%, and the elements in cumulus minerals after TLS will be enriched to a variable degree from 15 to 45% (Fig. 20). However, these different degrees of TLS for moderately incompatible and compatible elements will be clearly less significant than for incompatible elements (grey field, Fig. 17): from 11 to 16% for D=0.5, 2 to 5% for D =0.8, and from -2 to -5% for D =1.2.

Testing the modeling results

The correlation between element contents and Mg# in pyroxenes or An# in plagioclase could be used to test the above theoretical modeling. In the MZ samples, Cr and Ni show positive correlation with Mg# for both clinopyroxene and orthopyroxene (Figs. 12, 13), indicating that the Cr and Ni contents in both minerals are predominantly controlled by crystal fractionation. For moderately incompatible elements, such as Mn and Sc, there are generally negative correlations with respect to Mg# in clinopyroxene and orthopyroxene. This is also true for Sr, Ba, Eu contents and An# in plagioclase (Figs. 12, 13, 14). Tanner *et al.* (2014) plotted these components against stratigraphic height in the northern limb of the Bushveld Complex and found a clear negative correlation between moderately incompatible elements and Mg# of pyroxenes and An# of plagioclase, similarly to our observations. We argue that magma differentiation may have controlled the abundances of these trace elements in the cumulus minerals, whereas TLS is not prominent, because the core-to-rim concentration gradients are not large and the degree of the TLS is not as extensive as the model calculations indicate. In the case of highly incompatible elements, there is much less correlation between the element contents and Mg# of pyroxenes or An# of plagioclase (Figs. 9, 10, 11). This is also consistent with the modeling results, indicating that these elements have been more extensively modified by the effects of TLS due to larger core-to-rim concentration gradients. Accordingly, our observations are consistent with the theoretical calculations that the degree of TLS varies and depends on bulk partition coefficients. This is consistent with the observation of Chen et al. (2017) in the Panzhihua cumulate rocks in China that the highly incompatible elements in cumulus minerals may have been modified by TLS whereas the TLS on compatible elements are less prominent.

There is a good positive correlation between whole-rock Zr and all REEs, Y, Ti, and Zr in Cpx (Fig. 16). We interpret that the variable degree of TLS is due to a different amount of primary trapped liquid and the final element abundances in clinopyroxene may have mainly been controlled by the TLS, with a lesser contribution from magma differentiation. In contrast, Sc and Mn do not correlate with whole-rock Zr (only Sc plotted in Fig. 16f), indicating smaller effects of TLS. For plagioclase, all LREEs (except Eu) show a good positive correlation with whole-rock Zr (Fig. 17), also indicating a dominant control by TLS. However, the Sr, Eu and Ba contents show poor correlation with whole-rock Zr (Fig. 17), implying that these elements in plagioclase are controlled mainly by magma differentiation with insignificant effects of TLS. These observations agree with the results of model calculations in that TLS seems to have a more important role in changing the contents of highly incompatible elements than those of moderately incompatible elements and the extent of TLS is positively correlated with the primary amount of trapped liquid. For orthopyroxene, negative correlations between most HREE and Mg# is not evident. Moreover, the positive correlation between HREE and whole-rock Zr is also absent (Fig. 18). We suggest that the core-rim equilibration is not as efficient as in the case of clinopyroxene and plagioclase, probably due to the smaller diffusion coefficients of REE in orthopyroxene than clinopyroxene and plagioclase (Cherniak & Liang, 2007).

Wilson *et al.* (1999) observed a positive correlation between whole-rock Zr and highly incompatible trace elements in orthopyroxene and proposed that the rocks with a higher proportion of trapped liquid will finally contain higher incompatible trace element abundances in cumulus minerals due to the TLS. Cawthorn (2013, 2015) reported a positive correlation between Ce in orthopyroxene and whole-rock Zr in the UCZ of the Bushveld Complex and proposed a similar interpretation for such a correlation. Accordingly, caution must be paid when using highly incompatible trace elements of cumulus minerals to reverse calculate the parental magma composition.

Constraining the parental magma composition of the Main Zone

Method

The parental magma composition is calculated based on partition coefficients and mineral compositions (cf. Lambert & Simmons, 1987; Mathez, 1995). The concentration of an element i in the liquid (C^{i}_{Liq}) from which a cumulus mineral formed was calculated by assuming chemical equilibrium between the mineral (Min) and the liquid (Liq) and using the following equation:

$C^i_{Liq} = C^i_{Min} / D^i$

where C^i_{Min} is the concentration of the element i in a cumulus mineral and D^i is the partition coefficient between the mineral and the liquid.

Compatible and moderately incompatible elements

As discussed above, the contents of compatible trace elements (Cr, Ni) and moderately incompatible elements (Mn, Sc, Ni, Sr, Ba, Eu) in cumulus minerals are less modified by the effects of TLS, and hence these elements could be used to directly calculate the magma composition based on the method described above. The partition coefficients are from the compilation of Bédard (2001), except for Mn (Le Roux *et al.*, 2011). As magma differentiation will change the abundances of these elements in the magma (e.g., Cr and Ni in clinopyroxene decrease and Sr, Eu, and Ba in plagioclase increase with magma fractionation), the most primitive samples with the highest compatible elements (e.g., Cr, Ni) and lowest moderately incompatible elements (Mn, Sc, Ba, Sr Eu) will be the best ones to estimate the parental magma composition for these elements.

B1 rocks clearly have higher Cr and Ni contents, but lower Sr and Eu contents than B2 and B3 rocks (Fig. 21). On the Cr vs. Ni and Ba vs. Sr diagrams, the calculated parental magma compositions are clearly different from the composition of B1, but plot within the fields of B2 and B3 (Figs. 22a, b). On the Eu vs. Sr diagram, the most primitive samples plot in the field of B3 but show lower Eu contents than B2 rocks (Fig. 21c). On the Mn vs. Sc diagram, the most primitive samples show higher Sc than B2 rocks but plot in the field of B3 rocks (Fig. 21d). In summary, it appears that the parental magma to the MZ has a closer chemical affinity to B3 than B1 and B2 marginal rocks.

Rare earth elements

The values of the adopted partition coefficients have a significant effect on the calculated results. In general, the trace element partition coefficients between a mineral and melt are dependent on pressure, temperature, and compositions of the mineral and melt (Wood & Blundy, 2003; and references therein). We use the method of Sun & Liang (2012) to calculate the partition coefficients of REE in clinopyroxene. Using the method of VanTongeren & Mathez (2013), we estimated the temperature of crystallization by the composition of plagioclase, yielding values from 1051 to 1126 ^{o}C. For orthopyroxene, we calculated the partition coefficients of REE based on measured Mg# of orthopyroxene, using the method of Bédard (2007). The calculated partition coefficients of REE for clinopyroxene and orthopyroxene are listed in Supplementary Data. They are generally comparable with than the recommendations of Bédard (2001). The calculated partition coefficients of HREEs in clinopyroxene and orthopyroxene are generally comparable to that of Bédard (2001), but that of LREEs are about 50% higher than Bédard (2001). For two samples (A1 and A238) with lower Mg# show higher partition coefficients of REEs for orthopyroxene. Accordingly, we use the combination of Bédard (2001) in our calculations, but note that if our calculated partition coefficients are employed the calculated REE contents of parental magma tend to be similar or slightly lower.

We calculated REE contents of the parental magma based on the REE contents of clinopyroxene, orthopyroxene and plagioclase and the respective partition coefficients. Some elements with abundances below or close to their detection limits were not used (e.g., HREE in plagioclase and LREE in orthopyroxene). The available mineral compositional data of MZ and UZ from Eastern Bushveld and Northern Bushveld were also used in the calculation (Tanner et al., 2014; VanTongeren & Mathez, 2013). We then compare the calculated results with the B2 and B3 marginal rocks using chondrite-normalized REE diagrams. As shown by Figs. 22 and 23, the calculated compositions for the MZ section from the different limbs show similar REE patterns. In Western Bushveld, the sample with the lowest whole-rock Zr content (A65) yielded the lowest REE abundances in the calculated parental magmas from all the three minerals. Whole-rock Zr data are not available for all samples from Northern and Eastern Bushveld, but the lower limit of REE abundances of the calculated parental magma are similar to that of the Western Bushveld. As the modeling suggests, a low primary fraction of trapped liquid may result in a low degree of TLS. Therefore, we suggest that the use of the sample with the lowest REE concentration may be the best approach to the real parental magma composition.

The HREE contents of the calculated parental magma obtained using orthopyroxene are lower than those obtained using clinopyroxene. One potential interpretation is that during post-cumulus processes (Figs. 22, 23), REEs are preferentially partitioned into clinopyroxene relative to orthopyroxene because of the presence of more flexible vacancies in clinopyroxene (Sun & Liang, 2013). The samples with lowest HREE plot within the field of B3 rocks, being lower in HREE than B2 rocks (Fig. 23). This indicates that the parental magma to the Bushveld MZ is compositionally similar to B3 type marginal rocks.

The parental magmas calculated from clinopyroxene are higher in REE than either B2 or B3 rocks but show a strong negative Eu anomaly which is comparable to the lower level of B2 and upper level of B3 (Fig. 22). Analogously, the LREE contents of parental magma calculated based on plagioclase plot towards the lower level of the B2 field, but the Eu contents are clearly lower than in the B2 rocks, plotting in the field of B3 rocks (Fig. 23). One potential interpretation is that there is a negative Eu anomaly in the parental magma from which the clinopyroxene and plagioclase grains crystallized, probably due to early fractionation of plagioclase. However, this is not supported by the absence of negative Eu in the chondrite-normalized patterns of all the three types of marginal rocks at Bushveld (Barnes et al., 2010). Another possible reason is that the effect of TLS on Eu both in clinopyroxene and plagioclase is less prominent than on other REEs because the bulk partition coefficient of Eu (~0.5) is higher than those of other REEs (~0.1–0.2). Nevertheless, the calculated REE abundances of the parental magmas even from the samples with the lowest whole-rock Zr content may be higher than the real magma compositions, given that there is still some TLS effect, though being low. This is supported by the fact that a core-to-rim increase in Ti is also observed in some plagioclase grains in sample A65 while such a zonation in REE abundances is weak. In addition, sample A65 is located in the upper portion of the MZ with relatively low An# in plagioclase and Mg# in pyroxenes compared to samples from the lower portion (Fig. 2), and therefore the incompatible elements abundances may have been elevated by crystal fractionation, which would in turn increase the REE abundances of the calculated parental magma. Taken all these aspects into consideration, the parental magma of MZ should have more likely a B3-type composition. Generally, the REE abundance of parental magma calculated from clinopyroxene is clearly much higher than that calculated from plagioclase or orthopyroxene (Figs. 22, 23), indicating that equilibrium of REE among different minerals may have not been reached. This is similar to the reported dis-equilibrium of REE between clinopyroxene and orthopyroxene in the LZ and LCZ rocks of the Bushveld Complex (Liang et al., 2013).

Involvement of the UCZ magma

Clinopyroxene and plagioclase in sample A297, which is located near the bottom of the MZ, has clearly higher LREE contents than the overlying samples (e.g., A271). The euhedral texture of orthopyroxene and the clear anhedral interstitial texture of clinopyroxene and plagioclase suggest that orthopyroxene is the sole cumulus mineral and clinopyroxene and plagioclase crystallized from trapped liquid. Orthopyroxene in this sample has higher Mg# (76) than in the overlying sample A271, indicating a relatively primitive magma from which the orthopyroxene crystallized. The plagioclase grains have slightly lower An# (63) than in sample A271 (68), indicating that the high LREE content of plagioclase in sample A297 is a result of advanced fractionation of trapped liquid. However, the clinopyroxene in this sample shows high Mg# (84) and also has unusually high LREE contents. Sample A297 does not have unusually high whole-rock Zr and Nb contents (7.1 and 0.57 ppm, respectively), and thus the high LREE content is not likely a result of a higher amount of primary trapped liquid and higher TLS. A more reasonable interpretation is that the parental magma of this sample has higher LREE than other samples. The degree of trace element enrichment in sample A297 compared to the overlying samples decrease in the order of La, Ce > Pr, Nd > Sm, Eu both for clinopyroxene and plagioclase (Figs. 6, 8), and the enrichment of HREE both in clinopyroxene and orthopyroxene is less prominent (Figs. 6, 7). This could potentially be explained by a parental magma that was more rich in LREE relative to HREE. Barnes *et al.* (2010) suggested that the parental magma of the UCZ is of the B2 type and that of the MZ is of the B3 type. The two magma types have comparable major element and minor element contents, but B2 has a more fractionated REE patterns rich in LREE. This is consistent with a model that the parental magma of sample A297 may have a contribution of the UCZ magma with a B2 affinity, whereas the parental magma of the overlying MZ is dominated by a B3-type magma, given the stratigraphic location of sample A297 near the contact between the UCZ and MZ. The MZ rocks are characterized by high initial Sr isotope compositions of up to 0.70905 (A271, Karykowski *et al.*, 2017), but the stratigraphically lower samples show a downward decrease in whole-rock initial Sr isotope ratios towards the Merensky Reef (Mitchell et al., 1990; Karykowski *et al.*, 2017). It is suggested that the UCZ magma was involved in the lower portion of the MZ (Mitchell et al., 1990; Karykowski *et al.*, 2017). If that is the case, the UCZ magma may have a contribution to at least ~300 m (e.g., A297) above the UCZ.

CONCLUSIONS

We have analyzed major and trace elements of orthopyroxene, clinopyroxene and plagioclase for samples from the Main Zone (MZ) of the Bushveld Complex to constrain the parental magma composition of the MZ. Crystal fractionation seems to be the dominant process in the MZ of the Bushveld Complex as revealed by the progressive upward decrease in Mg# of orthopyroxene. Crystallization of trapped liquid has occurred in the Main Zone as evidenced by the clear outward increase in Ti and decrease in An# plagioclase grains. Model calculations suggest that the extent of the trapped liquid shift (TLS) on different elements in the MZ is variable and depends on the bulk partition coefficients. The effects of the TLS are less prominent for compatible elements (e.g., Cr, Ni in pyroxenes) and moderately incompatible elements (e.g., Mn and Sc in pyroxenes, Ba, Sr, Eu in plagioclase) than for highly incompatible elements. The fraction of the primary trapped liquid shows positive correlation with the effects of the TLS. The weak intra-grain zonation for REEs in the main three minerals indicates fast diffusion rates between overgrown rims and cores. In the MZ, abundances of the most highly incompatible trace element in cumulus minerals, especially plagioclase and clinopyroxene have been modified by the TLS. Some moderately incompatible elements (e.g., Mn and Sc in pyroxenes, Ba, Sr, Eu in plagioclase) and compatible elements (e.g., Cr, Ni in pyroxenes) are less affected.

The parental magma composition estimated from compatible and moderately incompatible elements has a closer chemical affinity to B3-type marginal rocks than B1 and B2 rocks. The TLS may have elevated the REE contents of cumulus minerals. The parental magma composition calculated from the samples with the lowest whole-rock Zr contents are the best estimates, though still having higher REE than the real parental magma. We suggest that the parental magma to the Bushveld MZ is most likely akin to the B3-type marginal rocks. In the lower part of the MZ, there may have been some involvement of the UCZ magma.

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FIGURE CAPTIONS

Fig. 1. Simplified geological map of the Bushveld Complex.

Fig. 2. Sample locations in the stratigraphy, mineral proportion and compositional variation of the Main Zone (MZ) in terms of Mg# of clinopyroxene (Cpx) and orthopyroxene (Opx), An# of plagioclase (Plag). The subdivision of the MZ into two norite units (N-I, N-II) and four gabbronorite units (GB-I to GB-IV) based on Mitchell (1990). Opx Mg# data from Mitchell (1990) are also shown for comparison. The mineral proportion distribution is based on Mitchell (1990) and this study.

Fig. 3. Photomicrographs of samples analyzed from the Main Zone of Western

Bushveld. (a, b) Euhedral orthopyroxene with interstitial clinopyroxene and plagioclase near the bottom of the MZ, sample A297. (c) Typical 'granular' texture in the MZ, showing discrete crystals of clinopyroxene and orthopyroxene between plagioclase, sample A1. (d) Pigeonite transformed to orthopyroxene and clinopyroxene, sample A35. (e) Plagioclase inclusions enclosed in orthopyroxene, and other discrete plagioclase grains, sample A271. (f) Biotite at the boundary of pyroxene and plagioclase grains, sample A106. (g) Sample A65 showing the lowest biotite content. This sample also has the lowest whole-rock Zr among the analyzed MZ samples. (h) Interstitial iron oxide minerals in sample A238. Photographs a-e and g-h taken in transmitted and crossed polars, and f in transmitted light with parallel polars. Cpx, Opx, Pign, Plag, Bit indicate clinopyroxene, orthopyroxene, pigeonite, plagioclase, biotite, respectively.

Fig. 4. Whole-rock primitive mantle-normalized trace element patterns of cumulate rocks from the Main Zone. The data are from Maier *et al.* (2013). The compositions of the B1, B2 and B3 magmas are from Barnes *et al.* (2010). Normalization values are from McDonough & Sun (1995).

Fig. 5. Primitive mantle-normalized trace element patterns for orthopyroxene, clinopyroxene and plagioclase crystals analyzed from cumulate rocks from the Main Zone of Western Bushveld. The grey field represents analytical results from Quebec and the circles those from Espoo, Finland. Normalization values are from McDonough & Sun (1995).

Fig. 6. Variation of Mg# (%) and trace element contents in orthopyroxene with stratigraphic position in the Main Zone of Western Bushveld.

Fig. 7. Variation of Mg# (%) and trace element contents in clinopyroxene with stratigraphic position in the Main Zone of Western Bushveld.

Fig. 8. Variation of An# (%) and trace element contents in plagioclase with stratigraphic position in the Main Zone of Western Bushveld.

Fig. 9. Major and trace element compositions in cores and rims of cumulus orthopyroxene grains from the Main Zone of Western Bushveld. Each point indicates one grain.

Fig. 10. Major and trace element compositions in cores and rims of cumulus clinopyroxene grains from the Main Zone of Western Bushveld. Each point indicates one grain.

Fig. 11. Major and trace element compositions in cores and rims of cumulus plagioclase grains from the Main Zone of Western Bushveld. Each point indicates one grain.

Fig. 12. Traverse analyses of plagioclase grains from core to rim, or from rim to core to rim. The error bar is generally within the symbols (error bar of Ti and Ce shown). Note the clear variation of Ti and An from core to rim and the homogeneous distribution of other elements including REEs (Ce shown), Pb, Sr, and Ba. Opx, Cpx and Plag indicate orthopyroxene, clinopyroxene, plagioclase, respectively.

Fig. 13. Variation of compatible, moderately incompatible and highly incompatible trace element abundances in Opx as a function of Mg# in Opx. The data of Eastern and Northern Bushveld are from VanTongeren & Mathez (2013) and Tanner *et al.* (2014), respectively. The available data from the UZ of Eastern and Northern Bushveld samples are also plotted.

Fig. 14. Variation of compatible, moderately incompatible and highly

incompatible trace element abundances in Cpx as a function of Mg# in Cpx. The data of Eastern and Northern Bushveld are from VanTongeren & Mathez (2013) and Tanner *et al.* (2014), respectively. The available data from the UZ of Eastern and Northern Bushveld samples are also plotted.

Fig. 15. Variation of moderately incompatible and highly incompatible trace element abundances in Plag as a function of An# in Plag. Data of Eastern and Northern Bushveld are from VanTongeren & Mathez (2013) and Tanner *et al.* (2014), respectively. The available data from the UZ of Eastern and Northern Bushveld samples are also plotted.

Fig. 16. Variation of highly incompatible and moderately incompatible trace element abundances in Opx with whole-rock Zr content. Data of the available UZ samples of Eastern Bushveld are from VanTongeren (2011) and VanTongeren & Mathez (2013).

Fig. 17. Variation of highly incompatible and moderately incompatible trace element abundances in Cpx with whole-rock Zr content. Data of the available UZ samples of Eastern Bushveld are from VanTongeren (2011) and VanTongeren & Mathez (2013).

Fig. 18. Variation of highly incompatible and moderately incompatible trace element abundances in Plag with whole-rock Zr content. Data of the available UZ samples of Eastern Bushveld are from VanTongeren (2011) and VanTongeren & Mathez (2013).

Fig. 19. Model calculations of the change of concentrations of elements with different bulk partition coefficients in evolving trapped liquid during closed-system fractionation. The primary fraction of trapped liquid is assumed to range from 20 to 40%. C_{Liq} and C_o indicate the element contents in the evolving

trapped liquid and primary trapped liquid. The ratio C_{Liq}/C_o reflects the compositional change in the trapped liquid during fractionation. It is worth noting that the change in the concentrations is more prominent for highly incompatible elements than for moderately incompatible elements. Due to their bulk partition coefficient of slightly higher than 1.0, the concentration decrease of compatible elements (Cr, Ni) in the trapped liquid is not prominent.

Fig. 20. Model calculations of the degree of the trapped liquid shift (TLS). It is assumed that the concentration gradient between the core and overgrown rim has been completely homogenized. TLS (%) is defined as the degree of element enrichment in the final cumulus mineral compared to the element content in the primary cumulus core. It is worth noting that there is good positive correlation between TLS and the fraction of the primary trapped liquid for incompatible elements, whereas for compatible elements, the correlation is negative. TLS is clearly higher for highly incompatible elements than for moderately incompatible elements. The decrease of compatible elements is not prominent given that the bulk partition coefficients do not deviate much from 1.0.

Fig. 21. Parental magma compositions calculated from compatible and moderately incompatible element abundances in cumulus minerals. Data of Eastern and Northern Bushveld are from VanTongeren & Mathez (2013) and Tanner et al. (2014). The compositions of B1, B2 and B3 are also plotted for comparison based on data from Barnes *et al.* (2010). Most of the partition coefficients are from Bédard (2001), and the partition coefficient of Mn in clinopyroxene is from Le Roux *et al.* (2011). Available data of the UZ of Eastern and Northern Bushveld is also plotted.

Fig. 22. Chondrite-normalized REE patterns of the parental magma calculated using Cpx compositions. Data of Eastern and Northern Bushveld are from

VanTongeren and Mathez (2013) and Tanner *et al.* (2014). The patterns of B2 and B3 rocks are also plotted for comparison based on data from Barnes *et al.* (2010). Available data of the UZ of Eastern and Northern Bushveld is also plotted.

Fig. 23. Chondrite-normalized REE patterns of the parental magma calculated using plagioclase and orthopyroxene compositions. Data of Eastern and Northern Bushveld are from VanTongeren and Mathez (2013) and Tanner *et al.* (2014). The patterns of B2 and B3 rocks are also plotted for comparison based on data from Barnes *et al.* (2010). Available data of the UZ of Eastern and Northern Bushveld is also plotted.

TABLE CAPTIONS

Table 1. Whole-rock major and trace element data for samples from the MZ of Western Bushveld (data from Maier *et al.*, 2013).

Table 2. Average major and trace element compositions in orthopyroxene from the MZ of Western Bushveld.

Table 3. Average major and trace element compositions in clinopyroxene from the MZ of Western Bushveld.

Table 4. Average major and trace element compositions in clinopyroxene from the MZ of Western Bushveld.

Table 5. Traverse major elements analyses of plagioclase grains from the MZ of Western Bushveld.

Table 6. Traverse trace elements analyses of plagioclase grains from the MZ of Western Bushveld.

Table 7. Mineral proportions MZ samples from Western Bushveld determined by CIPW norms.

SUPPLEMENTARY DATA CAPTIONS

Supplementary data 1. Estimation of LA-ICP-MS detection limits, precision and accuracy based on NIST610 and NIST 612 standards determined at the LabMater Laboratory in the University of Quebec at Chicoutimi, Canada, and BHVO-2G and BCR-2G determined at the Geological Survey of Finland in Espoo, Finland.

Supplementary data 2. Original spot analyses of major and trace elements in orthopyroxene, clinopyroxene and plagioclase grains of 6 samples from the MZ of Western Bushveld. Major elements determined by microprobe and trace elements by LA-ICP-MS at the LabMater Laboratory in the University of Quebec at Chicoutimi, Canada.

Supplementary data 3. Original spot analyses of major and trace elements in orthopyroxene, clinopyroxene and plagioclase grains of 10 samples from the MZ of Western Bushveld. Major elements determined by microprobe and trace elements by LA-ICP-MS at the Geological Survey of Finland in Espoo, Finland.

Supplementary data 4. Correction of the whole-rock Zr content of one sample (A238) from Western Bushveld.

Supplementary data 5. Partition coefficients of Cpx and Opx calculated by the methods of Sun and Liang (2012) and Bédard (2007). Recommended values of Bédard (2001) are listed for comparison.