

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

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19 **ABSTRACT:**

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

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

46 We have calculated the composition of the parental magma of the MZ of
47 the Bushveld Complex. The compatible and moderately incompatible element
48 contents of the calculated parental liquid are generally similar to those of the
49 B3 marginal rocks, but different from the B1 and B2 marginal rocks. For the
50 highly incompatible elements, we suggest that the use of sample with the lowest
51 whole-rock Zr content and the least degree of TLS is the best approach to
52 obtain the parental magma composition. The HREE contents of the magma
53 calculated from orthopyroxene are similar to B3 rocks and lower than B2 rocks.
54 The calculated REE contents from clinopyroxene are generally significantly
55 higher than B2 or B3 rocks, and that from plagioclase are in the lower level of
56 B2 but slightly higher than B3. However, the calculated REE patterns from both
57 clinopyroxene and plagioclase show strong negative Eu anomalies, which are
58 at the lower level of B2 field and within the B3 field, respectively. We suggest
59 that Eu may be less affected by TLS than other REEs due to its higher bulk
60 compatibility. Based on this and the fact that the calculated REE contents of the

61 parental magma should be higher than the real magma composition due to
62 some degree of crystal fractionation and TLS even for the sample with the
63 lowest amount of trapped liquid, we propose that a B3 type liquid is the most
64 likely parental magma to the MZ of the Bushveld Complex. In the lowermost
65 part of the MZ, there is involvement of the Upper Critical Zone (UCZ) magma.

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

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72 INTRODUCTION

73

74 There have been different approaches to constrain the composition of the
75 parental liquid(s) to mafic layered intrusions. In many studies, the crystallization
76 history of the cumulate rocks have been modeled based on fine-grained contact
77 rocks or dikes and sills spatially associated with the intrusion (Cawthorn *et al.*,
78 1981; Sharpe, 1981; Davies & Tredoux, 1985; Harmer & Sharpe, 1985; Sharpe
79 & Hulbert, 1985; Curl, 2001; Cawthorn, 2006; Namur *et al.*, 2010; Barnes *et al.*,
80 2010; Seat *et al.*, 2011; Godel *et al.*, 2011b), but the contact rocks are often
81 contaminated. One way to estimate the bulk magma is to calculate the weighted
82 average composition of the cumulate rocks (e.g., Morse, 1981; VanTongeren *et al.*,
83 2010), but this requires comprehensive sampling and may lead to imprecise
84 results for intrusions that have behaved as an open system. Whole-rock mass
85 balance is used to estimate the parental magma composition of trace elements
86 assuming that the whole-rock trace element content represents the sum of the
87 concentrations of an element in the cumulus fraction and trapped liquid, with
88 the latter assumed to represent the melt composition (Cawthorn, 1991; Bédard
89 2001; Godel *et al.*, 2011a). However, the initial proportion of trapped liquid is
90 difficult to estimate if post-cumulus overgrowth has taken place (Godel *et al.*,

91 2011a). The fourth method, in-situ trace element analysis of silicate minerals
92 coupled with mineral/melt partition coefficients, could potentially be used to
93 calculate the trace element composition of magma (Bédard, 1994, 2001; Eales,
94 2000; Godel *et al.*, 2011a; VanTongeren & Mathez, 2013). However, the trace
95 element abundances of the cumulus minerals may have been modified by
96 effects of the trapped liquid shift (TLS) (Barnes, 1986; Mathez, 1995; Pun *et al.*,
97 1997; Wilson *et al.*, 1999; Godel *et al.*, 2011a; Tanner *et al.*, 2014; Chen *et al.*,
98 2017) or by inter-mineral diffusion (Tanner *et al.*, 2014), hampering the use of
99 in-situ trace element analyses for obtaining the original compositional
100 information on cumulus minerals. Yet, it is not well constrained how the
101 concentrations of different trace elements are modified.

102 Much attention has been paid to unravelling the composition of the parental
103 magmas to the Bushveld Complex in South Africa, the world's largest layered
104 intrusion containing more than 70% of the world's platinum-group element
105 (PGE) resources (Vermaak, 1995; Cawthorn, 1999) and a considerable
106 proportion of the global V and Cr resources (Polyak, 2010). Three types of
107 marginal rocks, designated as Bushveld 1–3 (B1–B3), are believed to be
108 representative of magmas that formed of the Bushveld Complex (Sharpe, 1981;
109 Harmer & Sharpe, 1985; Sharpe & Hulbert, 1985). The B1 rocks are chemically
110 magnesian andesites and spatially related to the Lower Zone (LZ) and Lower
111 Critical Zone (LCZ), while the B2 and B3 rocks are tholeiitic in composition and
112 underlie the Upper Critical Zone (UCZ) and Main Zone (MZ), respectively. The
113 B1 marginal rocks contain mainly orthopyroxene and minor olivine, and the B2
114 and B3 rocks are composed mainly of plagioclase, orthopyroxene, and
115 clinopyroxene (Barnes *et al.*, 2010). The B1 marginal rocks have been dated at
116 2050 ± 6 Ma, and a B2 rock has given an age of 2052 ± 6 Ma (Curl, 2001),
117 being similar to the ages of 2056.88 ± 0.41 Ma and 2057.04 ± 0.55 Ma
118 determined for the Merensky Reef in Western and Eastern Bushveld,
119 respectively (Scoates & Wall, 2015). Based on geochemistry, it has been
120 proposed that the LZ and LCZ were derived from a B1-type magma (Barnes *et*

121 al., 2010; Godel et al., 2011a).

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

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

142

143 GEOLOGICAL BACKGROUND

144

145 The Bushveld Igneous Complex in central Transvaal is exposed as the
146 western, eastern and northern lobes, covering an area of about 40,000 km²
147 (Cawthorn, 2015). Despite the huge size of the intrusion, recent high-precision
148 age determinations have provided evidence for a short time period of
149 emplacement and cooling of the whole ultramafic-mafic cumulate sequence
150 (the Rustenburg Layered Suite) within approximately one million years at 2.056

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

168 In the lower part of the MZ there are pyroxenite layers with euhedral
169 orthopyroxene occurring as the sole cumulus mineral and interstitial
170 clinopyroxene and plagioclase (sample A297, Figs. 3a, b). Most of the MZ rocks
171 show a granular texture, with subhedral crystals of clinopyroxene and
172 orthopyroxene occurring between plagioclase laths (Fig. 3c). The rocks typically
173 contain 10–30 vol% orthopyroxene, 20–30 vol% clinopyroxene, and 40–70 vol%
174 plagioclase (Fig. 3c). The low-Ca pyroxene is dominated by orthopyroxene, but
175 pigeonite occurs near the Pyroxenite Marker in the upper part of the MZ (Fig.
176 3d). In some cases, plagioclase grains are partly or entirely enclosed in
177 orthopyroxene, but rarely in clinopyroxene (Fig. 3e). The enclosed plagioclase
178 grains generally show a rounded shape and are smaller than other unenclosed
179 grains (Mitchell, 1990). In rare occurrences in the northern limb, clinopyroxene
180 has been reported to enclose orthopyroxene, which in turn enclose grains of

181 plagioclase (Roelofse *et al.*, 2012), suggesting a crystallization sequence of
182 plagioclase-orthopyroxene- clinopyroxene. In many samples, biotite occurs at
183 the boundary of pyroxene and plagioclase grains (Fig. 3f).

184

185 *Sampling and whole-rock geochemistry*

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

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

201

202 METHODS

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

210 Trace element concentrations of the minerals of 6 samples were analyzed

211 by laser-ablation inductively coupled mass spectrometry (LA-ICP-MS) at the
212 LabMater Laboratory in the University of Quebec at Chicoutimi (UQAC) using
213 a Thermo X7 mass spectrometer coupled with a New Wave Research 213 nm
214 Nd: YAG UV laser ablation system. The analyses were conducted using 80 μm
215 diameter spots, a laser frequency of 10 Hz, a power of 0.8 mJ/pulse, and He–
216 Ar carrier gas. The gas background was collected for 20 s followed by 60 s of
217 data acquisition. The ablated material was analyzed by ICP-MS operated in
218 time-resolved mode using peak jumping. NIST-610 reference material was
219 used for calibration and NIST-612 as a monitor (Godel *et al.*, 2011b). The results
220 of NIST-612 and detection limits are listed in online Supplementary Data. The
221 reduction of the data was computed using Plasma Lab software (Thermo
222 Elemental) and ^{29}Si as an internal standard (Godel *et al.*, 2011a). Trace element
223 concentrations of the minerals of 10 samples (6 have previously been analyzed
224 in Quebec) were analyzed at the Geological Survey of Finland (GTK) in Espoo
225 using an AttoM Single Collector High Resolution ICP-MS, coupled with Photon
226 MachinesTM deep UV (193 nm wavelength) excimer laser system. The
227 analyses were conducted using 50 μm diameter spots, a laser frequency of 10
228 Hz, a power of 4.68J/cm², and He-Ar carrier gas. The gas background was
229 collected for 20 s followed by 60 s of data acquisition. **BHVO-2G** reference
230 material was used for calibration and **BCR-2G** as a monitor. The reduction of
231 the data was computed using Glitter software and ^{29}Si as an internal standard.
232 The results of **BCR-2G** and detection limits are listed in online Supplementary
233 Data.

234

235 ANALYTICAL RESULTS

236

237 All data of spot analyses of orthopyroxene, clinopyroxene and plagioclase are
238 listed in Supplementary Data. The average values of several spots of the three
239 minerals are listed in Tables 2, 3, 4. The Mg# values [atomic $100 \cdot \text{Mg}/(\text{Mg}+\text{Fe})$]
240 of Opx and Cpx and the An# values [atomic $100 \cdot \text{Ca}/(\text{Ca}+\text{Na})$] of plagioclase

241 are based on microprobe data and all trace element compositions on LA-ICP-
242 MS analyses. The trace element concentrations obtained for the standards
243 deviate less than 5-10% from the recommended values both in the Quebec and
244 Espoo analyses. As the calibration standard **BHVO-2G** may be better than
245 NIST-610 (Liu et al., 2010), we only use the trace element data obtained in
246 Espoo for most of our discussion. However, the comparison analyses between
247 core and rim (not traverse analyses) determined in Quebec is also used for
248 discussion because the compositional comparison between core and rim of
249 mineral grains may have not been affected by calibration standard at all.

250

251 *Orthopyroxene*

252 The Mg# values of orthopyroxene range from 56.9 to 75.5. In general, Mg#
253 decreases upwards in the stratigraphy, excluding sample A238, and are
254 consistent with the results of Mitchell *et al.* (1998) (Fig. 2). The analyzed
255 orthopyroxene grains from the MZ have Cr contents in the range of 10–713
256 ppm and the Ni contents vary from 224 to 681 ppm. They have considerable
257 amounts of some other minor elements: Mn from 2600 to 4400 ppm, Sc from
258 34 to 47 ppm, and Co from 123 to 184 ppm. Of the three major silicate minerals
259 (orthopyroxene, clinopyroxene, plagioclase), orthopyroxene has the lowest
260 concentrations for most incompatible trace elements and are characterized by
261 relatively low LREE abundances compared to HREE, which is consistent with
262 the experimentally determined orthopyroxene/melt partition coefficients for
263 these elements (e.g., Bédard, 2001 and references therein) (Fig. 5). On the
264 primitive mantle-normalized multi-element plot presented in Fig. 5a, all
265 orthopyroxene compositions are depleted in Ba, Sr, Eu, but not in Zr and Hf,
266 and slightly enriched in U and Ti. Niobium was not plotted because its
267 abundance is close to the detection limit.

268

269 *Clinopyroxene*

270 The Mg# values in clinopyroxene range from 65.1 to 83.6 and correlate well

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

278

279 *Plagioclase*

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

286

287 *Compositional variation across stratigraphy*

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

301 show no clear correlation(Figs. 6, 7, 8).

302

303 *Intra-grain and inter-grain variation*

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

316 To better understand the mechanism of intra-grain chemical variation, we have
317 conducted rim-to-core or rim-to-core-to-rim traverse analyses of plagioclase
318 grains from two samples with different whole-rock Zr contents (Tables, 5, 6; Fig.
319 12). For most plagioclase grains, the outermost rim shows a sharp increase in
320 An# coupled with a sharp decrease in Ti (Fig. 12). However, excluding the
321 outermost rim, there is a clear progressive outward decrease in An# coupled
322 with an increase in Ti, with about 20-50% higher in cores than that of rims. In
323 contrast, there is much lower core-to-rim variation for LREEs (Ce shown) (Figs.
324 12a, b, c, d). For a couple of grains, the rim has about 15% higher Ce than the
325 core, but for most grains the elevation of Ce from core to rim is less than 10%.
326 For Sr, Ba and Pb, there is almost no core-rim variation. For a couple of grains,
327 there is complex variation of An# from core to rim, and it is worth noting that the
328 Ti contents always show negative correlation with An# but the other trace
329 elements (LREEs, Sr, Ba, Pb) do not show much variation (Figs. 12e, f).

330

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

336

337 *Correlation between element contents and degree of crystal fractionation*

338 The bulk-rock partition coefficient D of an element is dependent on the partition
339 coefficients of the element for different minerals and the proportions of these
340 minerals during crystallization. The partition coefficients of elements for
341 different minerals used in this work are from the compilation of Bédard (2001),
342 and the bulk partition coefficients are estimated assuming that the modal
343 percentages of plagioclase, orthopyroxene and clinopyroxene are 50%, 25%,
344 and 25%, respectively, based on our CIPW calculations (Table 7) and Mitchell
345 (1990) (Fig. 2). Chrome and Ni are compatible in both clinopyroxene and
346 orthopyroxene, and their calculated bulk partition coefficients in the Bushveld
347 MZ are slightly higher than 1 ($D=1.2$). Manganese, Sc, and Zn are compatible
348 in orthopyroxene and clinopyroxene, but highly incompatible in plagioclase.
349 Due to the high abundance of plagioclase, the bulk partition coefficients of these
350 elements are lower than 1 ($D = 0.5$) and thus the elements are moderately
351 incompatible. Strontium is compatible in plagioclase, whereas Ba and Eu are
352 moderately incompatible in plagioclase, with their bulk partition coefficients
353 falling slightly below 1 ($D = 0.5$ to 0.8). For REEs, Zr, Hf, and Ti, the bulk D
354 values range from 0.1 to 0.2 and for Nb, D is <0.01 , making these elements
355 highly incompatible.

356 To assess whether these elements behave systematically, we plotted
357 different elements in pyroxenes against their Mg# and those in plagioclase
358 against An# using our data from the Western Bushveld MZ coupled with data
359 from the Eastern Bushveld MZ and Northern Bushveld MZ published by
360 VanTongeren & Mathez (2013) and Tanner *et al.* (2014), respectively (Figs. 13,

361 14, 15). Available data from the UZ of Eastern and Northern Bushveld is also
362 plotted (VanTongeren & Mathez, 2013; Tanner *et al.*, 2014). There is generally
363 a positive correlation between Mg# and the compatible elements contents of
364 both orthopyroxene and clinopyroxene (e.g., Cr, Ni; Figs. 13, 14). For
365 moderately incompatible elements, a broadly negative correlation with respect
366 to Mg# or An# is observed (e.g., Mn, Sc, Sr, Ba, Eu; Figs. 13, 14, 15). On the
367 Ni vs. Mg# and Sc vs. Mg# diagrams of clinopyroxene, two samples from the
368 MZ of Eastern Bushveld plot away from the main trend, but they are
369 anorthosites (Figs. 14b, d). Samples from the UZ broadly plot on the same trend
370 as the MZ samples. However, for highly incompatible elements, there is much
371 poorer correlation with Mg# or An#.

372

373 *Correlation with whole-rock Zr contents*

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

391

392 *The lower portion of the MZ*

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

410

411 DISCUSSION

412

413 *Fractional crystallization*

414

415 Mitchell *et al.* (1990) carried out a systematic study of the mineralogy and
416 mineral compositions of the MZ of Western Bushveld. Based on the progressive
417 upwards decreasing Mg# of orthopyroxene with minor compositional reversals,
418 the authors concluded that the MZ below the Pyroxene Marker in Western
419 Bushveld is dominated by crystal fractionation with minor magma
420 replenishments (Fig. 2). Our new compositional data on orthopyroxene (e.g.,

421 Mg#) are broadly consistent with the variation trend of Mg# presented by
422 Mitchell *et al.* (1990). Crystal fractionation is also supported by the variation of
423 Mg# in clinopyroxene, compatible elements (e.g., Cr, Ni in both orthopyroxene
424 and clinopyroxene), moderately incompatible elements (e.g., Mn, Sc of both
425 clinopyroxene and orthopyroxene, and Sr, Ba, Eu of plagioclase). However,
426 highly incompatible elements (e.g., REEs, Zr) in the three minerals show
427 decoupling from Mg# in orthopyroxene or An# in plagioclase (Fig. 6, 7, 8).

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

441

442 *Evolution of trapped liquid and diffusive modification*

443

444 The crystallization of trapped interstitial liquid depends on the mobility of the
445 liquid and the permeability of the crystal mush. Adcumulus-style crystallization
446 occurs if there is a high permeability of the crystal mush, allowing evolving
447 intercumulus liquid to maintain communication with the liquid in the main
448 magma reservoir by diffusion and/or convection, and if compaction, annealing,
449 and grain boundary re-adjustment take place (e.g., McKenzie, 1984; Kerr & Tait,
450 1986; Tait & Jaupart, 1992; Tegner *et al.*, 2009). On the other hand,

451 orthocumulus-style crystallization will operate if the circulation of the interstitial
452 liquid is not efficient, involving overgrowth of primocrysts and evolved interstitial
453 phases that crystallized from the trapped liquid. The Bushveld MZ rocks more
454 likely crystallized as an orthocumulate system with considerable interstitial
455 liquid fractionation, which is reflected by overgrowth textures of cumulus
456 minerals (Mitchell *et al.*, 1990; this study). In such a system, core-to-rim
457 variation of An# in plagioclase would be expected, as An# of plagioclase is
458 considered resistant to diffusive modification under magmatic conditions due to
459 the slow charge-coupled substitution of CaAl with NaSi (Grove *et al.*, 1984;
460 Morse, 1984, 2008; Cherniak, 2003; Tegner & Cawthorn, 2010). Also, zonation
461 of incompatible trace elements in cumulus minerals would be present as these
462 elements tend to increase during the fractionation of trapped liquid in a relatively
463 closed system (Humphreys *et al.*, 2009; Godel *et al.*, 2011a). Because of its
464 slow diffusion, Ti in plagioclase is a good parameter for recording the evolution
465 of interstitial liquid (Humphreys *et al.*, 2009). In the Bushveld MZ, there is an up
466 to two-fold intra-grain scale difference in the Ti content of plagioclase grains.
467 Some grains show a higher Ti content in the rim than in the core, fitting well with
468 a process of trapped liquid crystallization (Fig. 11). However, some plagioclase
469 rims show a lower Ti content than the corresponding cores. In the Skaergaard
470 intrusion, the decreasing trend of Ti in plagioclase towards the rim has been
471 interpreted to reflect the onset of magnetite crystallization in the trapped liquid,
472 which occurred when the An# value of plagioclase decreased down to about 55
473 (Humphreys *et al.*, 2009). This is not applicable to our samples because of the
474 scarcity of magnetite.

475 Traverse analyses of plagioclase grains further show that many grains have
476 a sharp increase of An coupled with a sharp decrease of Ti in the outermost rim
477 of plagioclase grains (Fig. 12). This cannot be explained by percolation of
478 interstitial melt as this melt is normally is rather evolved and should produce a
479 lower An# value and higher Ti content in plagioclase. Nevertheless, it explains
480 why some rims show lower Ti than cores (Fig. 11). However, if not considering

481 the outmost part of plagioclase grains, a clear outward decrease in An# coupled
482 with an increase in Ti is observed for many plagioclase grains, providing robust
483 evidence for crystallization of trapped interstitial liquid (Fig. 12a, b, c, d).
484 Zonation of Ti has been reported both in orthopyroxene and clinopyroxene from
485 the LZ and LCZ of the Bushveld Complex (Godel et al., 2011a) and the Mont
486 de Crystal intrusion (Maier et al., 2015), which is interpreted as closed-system
487 crystallization of the trapped liquid with progressively enriched incompatible
488 element contents in the liquid. For a few grains, the complex zonation of An#
489 from core to rim may reflect re-adjustment of crystal boundaries (Boudreau,
490 1999), however, the negative correlation between An# and Ti indicates
491 overgrowth of plagioclase from trapped liquid also occurred for these grains
492 (Figs. 12e, f).

493 Because the bulk-rock partition coefficients of other elements (e.g., REE,
494 Pb) are comparable to that of Ti, the element enrichments in the evolving
495 trapped liquid should be at a similar level. However, traverse analyses of
496 plagioclase grains of these elements show much lower core-to-rim variation,
497 which is clearly different from the behavior of Ti (Fig. 12). This is consistent with
498 the small intra-grain-scale variation of REEs in plagioclase revealed by core-
499 rim associations, which is clearly much lower than that of Ti (Fig. 11). In addition,
500 the inter-grain variation of REE within the thin-section scale is clearly lower than
501 that of Ti, with a relative standard derivation of about 5% (1σ) for REEs and
502 about 15% (1σ) for Ti (Fig. 8). The contrasting behavior of REEs and Ti in the
503 Bushveld MZ samples provides a strong argument that the diffusion rate of
504 REEs in plagioclase is faster than that of Ti. Experimental studies suggest that
505 the diffusion rate of an element in plagioclase is highly dependent on the charge
506 of the cation, with the univalent cations diffusing faster than the divalent cations
507 and the latter in turn faster than the trivalent cations (Charniak, 2003). Though
508 there are no direct experiment data for diffusion of Ti, as a quadrivalent cation,
509 it likely diffuses slower than the trivalent REEs (Charniak, 2003). In contrast, in
510 the ~2.44 Ga mafic dikes in the Fennoscandia Shield, 2- to 3-fold core-to-rim

511 enrichment in REEs and Ti has been observed in clinopyroxene grains (our
512 unpublished data). A core-to-rim variation of REE has also been reported in
513 clinopyroxene of the Rum intrusion (Leuthold *et al.*, 2014). Because the cooling
514 rate in mafic dike and small intrusion (e.g., Rum) is faster than that in large
515 intrusions like Bushveld, we suggest that the chemical zonation produced by
516 closed-system crystal fractionation in the former is generally quenched due to
517 fast cooling, whereas the concentration gradients between core and rim may
518 have been erased in Bushveld by diffusion of REEs.

519

520 ***Quantitative modeling of the final trapped liquid composition***

521 During the solidification of mafic crystal mushes, the crystal framework is
522 thought to contain 40–70% of trapped liquid (e.g., Shirley, 1986; Philpotts &
523 Carroll, 1996; Philpotts *et al.*, 1998; Jerram *et al.*, 1996, 2003; Donev *et al.*,
524 2004). We assume a two-stage process in which the overgrowth of crystals is
525 faster than the element diffusion: 1) During closed-system fractionation of
526 trapped liquid with overgrowth of cumulus minerals, the incompatible elements
527 tend to increase in the evolving trapped liquid, resulting in increasing element
528 contents in the rim, which is similar to the observed enrichment trend in mafic
529 dikes; 2) Due to the chemical potential gradient between the core and rim in
530 cumulus minerals, there could be subsequent diffusion of these elements
531 (Godel *et al.*, 2011a, Tanner *et al.*, 2014).

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

$$539 C_{\text{Liq}} = C_0 F^{(D-1)}$$

540 in which C_0 and C_{Liq} are the element contents in the primary trapped liquid and

541 the evolving trapped liquid, respectively, and F is the initial fraction of the
 542 trapped liquid. The partition coefficients of elements in different minerals are
 543 from Bédard (2001). The bulk partition coefficients D are estimated assuming
 544 the approximate mineral fractions of plagioclase, orthopyroxene and
 545 clinopyroxene to be 0.5, 0.25, and 0.25, respectively, based on the calculated
 546 CIPW norms (Table 5).

547 We use C_{Liq}/C_0 to reflect the compositional change between the
 548 fractionating trapped liquid and the primary trapped liquid. The fraction of
 549 primary trapped liquid is assumed to be from 20 to 40%. The C_{Liq}/C_0 ratio is
 550 calculated to be the following for elements with different bulk partition
 551 coefficients: 1) about 0.3 to 0.6 for compatible elements with D from 1.5 to 1.2;
 552 2) 1.6 to 3.2 for moderately incompatible elements with D from 0.8 to 0.5; 3) 6.3
 553 to 7.9 for incompatible elements with D from 0.2 to 0.1 (Fig. 19), and 4) about
 554 10 for highly incompatible elements with D of about 0.01 (not shown). It is
 555 clearly that the enrichment of elements in the fractionated trapped liquid is
 556 negatively correlated with the bulk partition coefficients, with the highest
 557 enrichment for the most incompatible elements.

558

559 *Modeling the degree of trapped liquid shift*

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

$$566 \quad C_{Rim} = (\int C_{Liq} \times D \, dF_{Rim}) / F_{Rim} \quad (2)$$

$$567 \quad C_{Final} = (C_{Rim} \times F_{Rim} + C_{Core} \times F_{Core}) / (F_{Rim} + F_{Core}) \quad (3)$$

$$568 \quad \text{Trapped liquid shift (TLS) (\%)} = (C_{Final} - C_{Core}) / C_{Core} \times 100 \quad (4)$$

569 F_{Rim} is the fraction of overgrown rim and dF_{Rim} is differential calculus of
 570 overgrown rim. D is bulk partition coefficient. C_{Core} and C_{Rim} are the element

571 contents in the primary core and overgrown rim with changing composition,
572 respectively, and C_{Final} is the final content after core-rim homogenization.

573 The calculated results show that the REE contents in cumulus minerals after
574 TLS will be about 25 to 35% higher than the primary core compositions for
575 elements with bulk partition coefficients of 0.2 to 0.1, respectively, if we assume
576 that the primary trapped liquid fraction was 30%. For moderately incompatible
577 elements with bulk partition coefficients from 0.8 to 0.5, the bulk cumulate
578 contents will be enriched by 4–13%. For compatible elements, such as Cr and
579 Ni, the final concentrations in clinopyroxene and orthopyroxene could be about
580 1 to 7% lower than the original contents, assuming a bulk partition coefficient
581 of 1.2. From the calculation presented above, the concentrations in the final
582 cumulus minerals have been modified variably by TLS, depending on the bulk
583 partition coefficient, with the TLS of incompatible elements being clearly more
584 intensive than that of moderately incompatible elements and compatible
585 elements.

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

596

597 *Testing the modeling results*

598 The correlation between element contents and Mg# in pyroxenes or An# in
599 plagioclase could be used to test the above theoretical modeling. In the MZ
600 samples, Cr and Ni show positive correlation with Mg# for both clinopyroxene

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

624 There is a good positive correlation between whole-rock Zr and all REEs,
625 Y, Ti, and Zr in Cpx (Fig. 16). We interpret that the variable degree of TLS is
626 due to a different amount of primary trapped liquid and the final element
627 abundances in clinopyroxene may have mainly been controlled by the TLS, with
628 a lesser contribution from magma differentiation. In contrast, Sc and Mn do not
629 correlate with whole-rock Zr (only Sc plotted in Fig. 16f), indicating smaller
630 effects of TLS. For plagioclase, all LREEs (except Eu) show a good positive

631 correlation with whole-rock Zr (Fig. 17), also indicating a dominant control by
632 TLS. However, the Sr, Eu and Ba contents show poor correlation with whole-
633 rock Zr (Fig. 17), implying that these elements in plagioclase are controlled
634 mainly by magma differentiation with insignificant effects of TLS. These
635 observations agree with the results of model calculations in that TLS seems to
636 have a more important role in changing the contents of highly incompatible
637 elements than those of moderately incompatible elements and the extent of
638 TLS is positively correlated with the primary amount of trapped liquid. For
639 orthopyroxene, negative correlations between most HREE and Mg# is not
640 evident. Moreover, the positive correlation between HREE and whole-rock Zr is
641 also absent (Fig. 18). We suggest that the core-rim equilibration is not as
642 efficient as in the case of clinopyroxene and plagioclase, probably due to the
643 smaller diffusion coefficients of REE in orthopyroxene than clinopyroxene and
644 plagioclase (Cherniak & Liang, 2007).

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

654

655 Constraining the parental magma composition of the Main Zone

656

657 *Method*

658 The parental magma composition is calculated based on partition coefficients
659 and mineral compositions (cf. Lambert & Simmons, 1987; Mathez, 1995). The
660 concentration of an element *i* in the liquid (C_{Liq}^i) from which a cumulus mineral

661 formed was calculated by assuming chemical equilibrium between the mineral
662 (Min) and the liquid (Liq) and using the following equation:

$$663 \quad C_{\text{Liq}}^i = C_{\text{Min}}^i / D^i$$

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

666

667 *Compatible and moderately incompatible elements*

668 As discussed above, the contents of compatible trace elements (Cr, Ni) and
669 moderately incompatible elements (Mn, Sc, Ni, Sr, Ba, Eu) in cumulus minerals
670 are less modified by the effects of TLS, and hence these elements could be
671 used to directly calculate the magma composition based on the method
672 described above. The partition coefficients are from the compilation of Bédard
673 (2001), except for Mn (Le Roux *et al.*, 2011). As magma differentiation will
674 change the abundances of these elements in the magma (e.g., Cr and Ni in
675 clinopyroxene decrease and Sr, Eu, and Ba in plagioclase increase with magma
676 fractionation), the most primitive samples with the highest compatible elements
677 (e.g., Cr, Ni) and lowest moderately incompatible elements (Mn, Sc, Ba, Sr Eu)
678 will be the best ones to estimate the parental magma composition for these
679 elements.

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

689

690 *Rare earth elements*

691

692 The values of the adopted partition coefficients have a significant effect on the
693 calculated results. In general, the trace element partition coefficients between
694 a mineral and melt are dependent on pressure, temperature, and compositions
695 of the mineral and melt (Wood & Blundy, 2003; and references therein). We use
696 the method of Sun & Liang (2012) to calculate the partition coefficients of REE
697 in clinopyroxene. Using the method of VanTongeren & Mathez (2013), we
698 estimated the temperature of crystallization by the composition of plagioclase,
699 yielding values from 1051 to 1126 °C. For orthopyroxene, we calculated the
700 partition coefficients of REE based on measured Mg# of orthopyroxene, using
701 the method of Bédard (2007). The calculated partition coefficients of REE for
702 clinopyroxene and orthopyroxene are listed in Supplementary Data. They are
703 generally comparable with than the recommendations of Bédard (2001). The
704 calculated partition coefficients of HREEs in clinopyroxene and orthopyroxene
705 are generally comparable to that of Bédard (2001), but that of LREEs are about
706 50% higher than Bédard (2001). For two samples (A1 and A238) with lower
707 Mg# show higher partition coefficients of REEs for orthopyroxene. Accordingly,
708 we use the combination of Bédard (2001) in our calculations, but note that if our
709 calculated partition coefficients are employed the calculated REE contents of
710 parental magma tend to be similar or slightly lower.

711 We calculated REE contents of the parental magma based on the REE
712 contents of clinopyroxene, orthopyroxene and plagioclase and the respective
713 partition coefficients. Some elements with abundances below or close to their
714 detection limits were not used (e.g., HREE in plagioclase and LREE in
715 orthopyroxene). The available mineral compositional data of MZ and UZ from
716 Eastern Bushveld and Northern Bushveld were also used in the calculation
717 (Tanner et al., 2014; VanTongeren & Mathez, 2013). We then compare the
718 calculated results with the B2 and B3 marginal rocks using chondrite-
719 normalized REE diagrams. As shown by Figs. 22 and 23, the calculated
720 compositions for the MZ section from the different limbs show similar REE

721 patterns. In Western Bushveld, the sample with the lowest whole-rock Zr
722 content (A65) yielded the lowest REE abundances in the calculated parental
723 magmas from all the three minerals. Whole-rock Zr data are not available for
724 all samples from Northern and Eastern Bushveld, but the lower limit of REE
725 abundances of the calculated parental magma are similar to that of the Western
726 Bushveld. As the modeling suggests, a low primary fraction of trapped liquid
727 may result in a low degree of TLS. Therefore, we suggest that the use of the
728 sample with the lowest REE concentration may be the best approach to the real
729 parental magma composition.

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

738 The parental magmas calculated from clinopyroxene are higher in REE
739 than either B2 or B3 rocks but show a strong negative Eu anomaly which is
740 comparable to the lower level of B2 and upper level of B3 (Fig. 22). Analogously,
741 the LREE contents of parental magma calculated based on plagioclase plot
742 towards the lower level of the B2 field, but the Eu contents are clearly lower
743 than in the B2 rocks, plotting in the field of B3 rocks (Fig. 23). One potential
744 interpretation is that there is a negative Eu anomaly in the parental magma from
745 which the clinopyroxene and plagioclase grains crystallized, probably due to
746 early fractionation of plagioclase. However, this is not supported by the absence
747 of negative Eu in the chondrite-normalized patterns of all the three types of
748 marginal rocks at Bushveld (Barnes et al., 2010). Another possible reason is
749 that the effect of TLS on Eu both in clinopyroxene and plagioclase is less
750 prominent than on other REEs because the bulk partition coefficient of Eu (~0.5)

751 is higher than those of other REEs (~0.1–0.2). Nevertheless, the calculated
752 REE abundances of the parental magmas even from the samples with the
753 lowest whole-rock Zr content may be higher than the real magma compositions,
754 given that there is still some TLS effect, though being low. This is supported by
755 the fact that a core-to-rim increase in Ti is also observed in some plagioclase
756 grains in sample A65 while such a zonation in REE abundances is weak. In
757 addition, sample A65 is located in the upper portion of the MZ with relatively
758 low An# in plagioclase and Mg# in pyroxenes compared to samples from the
759 lower portion (Fig. 2), and therefore the incompatible elements abundances
760 may have been elevated by crystal fractionation, which would in turn increase
761 the REE abundances of the calculated parental magma. Taken all these
762 aspects into consideration, the parental magma of MZ should have more likely
763 a B3-type composition. Generally, the REE abundance of parental magma
764 calculated from clinopyroxene is clearly much higher than that calculated from
765 plagioclase or orthopyroxene (Figs. 22, 23), indicating that equilibrium of REE
766 among different minerals may have not been reached. This is similar to the
767 reported dis-equilibrium of REE between clinopyroxene and orthopyroxene in
768 the LZ and LCZ rocks of the Bushveld Complex (Liang et al., 2013).

769

770 *Involvement of the UCZ magma*

771

772 Clinopyroxene and plagioclase in sample A297, which is located near the
773 bottom of the MZ, has clearly higher LREE contents than the overlying samples
774 (e.g., A271). The euhedral texture of orthopyroxene and the clear anhedral
775 interstitial texture of clinopyroxene and plagioclase suggest that orthopyroxene
776 is the sole cumulus mineral and clinopyroxene and plagioclase crystallized from
777 trapped liquid. Orthopyroxene in this sample has higher Mg# (76) than in the
778 overlying sample A271, indicating a relatively primitive magma from which the
779 orthopyroxene crystallized. The plagioclase grains have slightly lower An# (63)
780 than in sample A271 (68), indicating that the high LREE content of plagioclase

781 in sample A297 is a result of advanced fractionation of trapped liquid. However,
782 the clinopyroxene in this sample shows high Mg# (84) and also has unusually
783 high LREE contents. Sample A297 does not have unusually high whole-rock Zr
784 and Nb contents (7.1 and 0.57 ppm, respectively), and thus the high LREE
785 content is not likely a result of a higher amount of primary trapped liquid and
786 higher TLS. A more reasonable interpretation is that the parental magma of this
787 sample has higher LREE than other samples. The degree of trace element
788 enrichment in sample A297 compared to the overlying samples decrease in the
789 order of La, Ce > Pr, Nd > Sm, Eu both for clinopyroxene and plagioclase
790 (Figs. 6, 8), and the enrichment of HREE both in clinopyroxene and
791 orthopyroxene is less prominent (Figs. 6, 7). This could potentially be explained
792 by a parental magma that was more rich in LREE relative to HREE. Barnes *et al.*
793 *al.* (2010) suggested that the parental magma of the UCZ is of the B2 type and
794 that of the MZ is of the B3 type. The two magma types have comparable major
795 element and minor element contents, but B2 has a more fractionated REE
796 patterns rich in LREE. This is consistent with a model that the parental magma
797 of sample A297 may have a contribution of the UCZ magma with a B2 affinity,
798 whereas the parental magma of the overlying MZ is dominated by a B3-type
799 magma, given the stratigraphic location of sample A297 near the contact
800 between the UCZ and MZ. The MZ rocks are characterized by high initial Sr
801 isotope compositions of up to 0.70905 (A271, Karykowski *et al.*, 2017), but the
802 stratigraphically lower samples show a downward decrease in whole-rock initial
803 Sr isotope ratios towards the Merensky Reef (Mitchell *et al.*, 1990; Karykowski
804 *et al.*, 2017). It is suggested that the UCZ magma was involved in the lower
805 portion of the MZ (Mitchell *et al.*, 1990; Karykowski *et al.*, 2017). If that is the
806 case, the UCZ magma may have a contribution to at least ~300 m (e.g., A297)
807 above the UCZ.

808

809 CONCLUSIONS

810

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

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

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841

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1155

1156 FIGURE CAPTIONS

1157

1158 Fig. 1. Simplified geological map of the Bushveld Complex.

1159

1160 Fig. 2. Sample locations in the stratigraphy, mineral proportion and
1161 compositional variation of the Main Zone (MZ) in terms of Mg# of clinopyroxene
1162 (Cpx) and orthopyroxene (Opx), An# of plagioclase (Plag). The subdivision of
1163 the MZ into two norite units (N-I, N-II) and four gabbro-norite units (GB-I to GB-
1164 IV) based on Mitchell (1990). Opx Mg# data from Mitchell (1990) are also shown
1165 for comparison. The mineral proportion distribution is based on Mitchell (1990)
1166 and this study.

1167

1168 Fig. 3. Photomicrographs of samples analyzed from the Main Zone of Western

1169 Bushveld. (a, b) Euhedral orthopyroxene with interstitial clinopyroxene and
1170 plagioclase near the bottom of the MZ, sample A297. (c) Typical 'granular'
1171 texture in the MZ, showing discrete crystals of clinopyroxene and
1172 orthopyroxene between plagioclase, sample A1. (d) Pigeonite transformed to
1173 orthopyroxene and clinopyroxene, sample A35. (e) Plagioclase inclusions
1174 enclosed in orthopyroxene, and other discrete plagioclase grains, sample A271.
1175 (f) Biotite at the boundary of pyroxene and plagioclase grains, sample A106. (g)
1176 Sample A65 showing the lowest biotite content. This sample also has the lowest
1177 whole-rock Zr among the analyzed MZ samples. (h) Interstitial iron oxide
1178 minerals in sample A238. Photographs a-e and g-h taken in transmitted and
1179 crossed polars, and f in transmitted light with parallel polars. Cpx, Opx, Pign,
1180 Plag, Bit indicate clinopyroxene, orthopyroxene, pigeonite, plagioclase, biotite,
1181 respectively.

1182

1183 Fig. 4. Whole-rock primitive mantle-normalized trace element patterns of
1184 cumulate rocks from the Main Zone. The data are from Maier *et al.* (2013). The
1185 compositions of the B1, B2 and B3 magmas are from Barnes *et al.* (2010).
1186 Normalization values are from McDonough & Sun (1995).

1187

1188 Fig. 5. Primitive mantle-normalized trace element patterns for orthopyroxene,
1189 clinopyroxene and plagioclase crystals analyzed from cumulate rocks from the
1190 Main Zone of Western Bushveld. The grey field represents analytical results
1191 from Quebec and the circles those from Espoo, Finland. Normalization values
1192 are from McDonough & Sun (1995).

1193

1194 Fig. 6. Variation of Mg# (%) and trace element contents in orthopyroxene with
1195 stratigraphic position in the Main Zone of Western Bushveld.

1196

1197 Fig. 7. Variation of Mg# (%) and trace element contents in clinopyroxene with
1198 stratigraphic position in the Main Zone of Western Bushveld.

1199

1200 Fig. 8. Variation of An# (%) and trace element contents in plagioclase with
1201 stratigraphic position in the Main Zone of Western Bushveld.

1202

1203 Fig. 9. Major and trace element compositions in cores and rims of cumulus
1204 orthopyroxene grains from the Main Zone of Western Bushveld. Each point
1205 indicates one grain.

1206

1207 Fig. 10. Major and trace element compositions in cores and rims of cumulus
1208 clinopyroxene grains from the Main Zone of Western Bushveld. Each point
1209 indicates one grain.

1210

1211 Fig. 11. Major and trace element compositions in cores and rims of cumulus
1212 plagioclase grains from the Main Zone of Western Bushveld. Each point
1213 indicates one grain.

1214

1215 Fig. 12. Traverse analyses of plagioclase grains from core to rim, or from rim to
1216 core to rim. The error bar is generally within the symbols (error bar of Ti and Ce
1217 shown). Note the clear variation of Ti and An from core to rim and the
1218 homogeneous distribution of other elements including REEs (Ce shown), Pb,
1219 Sr, and Ba. Opx, Cpx and Plag indicate orthopyroxene, clinopyroxene,
1220 plagioclase, respectively.

1221

1222 Fig. 13. Variation of compatible, moderately incompatible and highly
1223 incompatible trace element abundances in Opx as a function of Mg# in Opx.
1224 The data of Eastern and Northern Bushveld are from VanTongeren & Mathez
1225 (2013) and Tanner *et al.* (2014), respectively. The available data from the UZ of
1226 Eastern and Northern Bushveld samples are also plotted.

1227

1228 Fig. 14. Variation of compatible, moderately incompatible and highly

1229 incompatible trace element abundances in Cpx as a function of Mg# in Cpx.
1230 The data of Eastern and Northern Bushveld are from VanTongeren & Mathez
1231 (2013) and Tanner *et al.* (2014), respectively. The available data from the UZ of
1232 Eastern and Northern Bushveld samples are also plotted.

1233

1234 Fig. 15. Variation of moderately incompatible and highly incompatible trace
1235 element abundances in Plag as a function of An# in Plag. Data of Eastern and
1236 Northern Bushveld are from VanTongeren & Mathez (2013) and Tanner *et al.*
1237 (2014), respectively. The available data from the UZ of Eastern and Northern
1238 Bushveld samples are also plotted.

1239

1240 Fig. 16. Variation of highly incompatible and moderately incompatible trace
1241 element abundances in Opx with whole-rock Zr content. Data of the available
1242 UZ samples of Eastern Bushveld are from VanTongeren (2011) and
1243 VanTongeren & Mathez (2013).

1244

1245 Fig. 17. Variation of highly incompatible and moderately incompatible trace
1246 element abundances in Cpx with whole-rock Zr content. Data of the available
1247 UZ samples of Eastern Bushveld are from VanTongeren (2011) and
1248 VanTongeren & Mathez (2013).

1249

1250 Fig. 18. Variation of highly incompatible and moderately incompatible trace
1251 element abundances in Plag with whole-rock Zr content. Data of the available
1252 UZ samples of Eastern Bushveld are from VanTongeren (2011) and
1253 VanTongeren & Mathez (2013).

1254

1255 Fig. 19. Model calculations of the change of concentrations of elements with
1256 different bulk partition coefficients in evolving trapped liquid during closed-
1257 system fractionation. The primary fraction of trapped liquid is assumed to range
1258 from 20 to 40%. C_{Liq} and C_o indicate the element contents in the evolving

1259 trapped liquid and primary trapped liquid. The ratio C_{Liq}/C_o reflects the
1260 compositional change in the trapped liquid during fractionation. It is worth noting
1261 that the change in the concentrations is more prominent for highly incompatible
1262 elements than for moderately incompatible elements. Due to their bulk partition
1263 coefficient of slightly higher than 1.0, the concentration decrease of compatible
1264 elements (Cr, Ni) in the trapped liquid is not prominent.

1265

1266 Fig. 20. Model calculations of the degree of the trapped liquid shift (TLS). It is
1267 assumed that the concentration gradient between the core and overgrown rim
1268 has been completely homogenized. TLS (%) is defined as the degree of
1269 element enrichment in the final cumulus mineral compared to the element
1270 content in the primary cumulus core. It is worth noting that there is good positive
1271 correlation between TLS and the fraction of the primary trapped liquid for
1272 incompatible elements, whereas for compatible elements, the correlation is
1273 negative. TLS is clearly higher for highly incompatible elements than for
1274 moderately incompatible elements. The decrease of compatible elements is not
1275 prominent given that the bulk partition coefficients do not deviate much from
1276 1.0.

1277

1278 Fig. 21. Parental magma compositions calculated from compatible and
1279 moderately incompatible element abundances in cumulus minerals. Data of
1280 Eastern and Northern Bushveld are from VanTongeren & Mathez (2013) and
1281 Tanner et al. (2014). The compositions of B1, B2 and B3 are also plotted for
1282 comparison based on data from Barnes *et al.* (2010). Most of the partition
1283 coefficients are from Bédard (2001), and the partition coefficient of Mn in
1284 clinopyroxene is from Le Roux *et al.* (2011). Available data of the UZ of Eastern
1285 and Northern Bushveld is also plotted.

1286

1287 Fig. 22. Chondrite-normalized REE patterns of the parental magma calculated
1288 using Cpx compositions. Data of Eastern and Northern Bushveld are from

1289 VanTongeren and Mathez (2013) and Tanner *et al.* (2014). The patterns of B2
1290 and B3 rocks are also plotted for comparison based on data from Barnes *et al.*
1291 (2010). Available data of the UZ of Eastern and Northern Bushveld is also
1292 plotted.

1293

1294 Fig. 23. Chondrite-normalized REE patterns of the parental magma calculated
1295 using plagioclase and orthopyroxene compositions. Data of Eastern and
1296 Northern Bushveld are from VanTongeren and Mathez (2013) and Tanner *et al.*
1297 (2014). The patterns of B2 and B3 rocks are also plotted for comparison based
1298 on data from Barnes *et al.* (2010). Available data of the UZ of Eastern and
1299 Northern Bushveld is also plotted.

1300

1301

1302 TABLE CAPTIONS

1303

1304 Table 1. Whole-rock major and trace element data for samples from the MZ of
1305 Western Bushveld (data from Maier *et al.*, 2013).

1306

1307 Table 2. Average major and trace element compositions in orthopyroxene from
1308 the MZ of Western Bushveld.

1309

1310 Table 3. Average major and trace element compositions in clinopyroxene from
1311 the MZ of Western Bushveld.

1312

1313 Table 4. Average major and trace element compositions in clinopyroxene from
1314 the MZ of Western Bushveld.

1315

1316 Table 5. Traverse major elements analyses of plagioclase grains from the MZ
1317 of Western Bushveld.

1318

1319 Table 6. Traverse trace elements analyses of plagioclase grains from the MZ of
1320 Western Bushveld.

1321

1322 Table 7. Mineral proportions MZ samples from Western Bushveld determined
1323 by CIPW norms.

1324

1325

1326

1327 SUPPLEMENTARY DATA CAPTIONS

1328

1329 Supplementary data 1. Estimation of LA-ICP-MS detection limits, precision and
1330 accuracy based on NIST610 and NIST 612 standards determined at the
1331 LabMater Laboratory in the University of Quebec at Chicoutimi, Canada, and
1332 **BHVO-2G** and **BCR-2G** determined at the Geological Survey of Finland in
1333 Espoo, Finland.

1334

1335 Supplementary data 2. Original spot analyses of major and trace elements in
1336 orthopyroxene, clinopyroxene and plagioclase grains of 6 samples from the MZ
1337 of Western Bushveld. Major elements determined by microprobe and trace
1338 elements by LA-ICP-MS at the LabMater Laboratory in the University of Quebec
1339 at Chicoutimi, Canada.

1340

1341 Supplementary data 3. Original spot analyses of major and trace elements in
1342 orthopyroxene, clinopyroxene and plagioclase grains of 10 samples from the
1343 MZ of Western Bushveld. Major elements determined by microprobe and trace
1344 elements by LA-ICP-MS at the Geological Survey of Finland in Espoo, Finland.

1345

1346 Supplementary data 4. Correction of the whole-rock Zr content of one sample
1347 (A238) from Western Bushveld.

1348

1349 Supplementary data 5. Partition coefficients of Cpx and Opx calculated by the
1350 methods of Sun and Liang (2012) and Bédard (2007). Recommended values
1351 of Bédard (2001) are listed for comparison.