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1 **Platinum-group element contents of Karelian kimberlites:**
2 **implications for the PGE budget of the sub-continental lithospheric**
3 **mantle**

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13

14 **Abstract.** We present high-precision isotope dilution data for Os, Ir, Ru, Pt, Pd and Re in Group I
15 and Group II kimberlites from the Karelian craton, as well as 2 samples of the Premier Group I
16 kimberlite pipe from the Kaapvaal craton. The samples have, on average, 1.38 ppb Pt and 1.33 ppb
17 Pd, with Pt/Pd around unity. These PGE levels are markedly lower, by as much as 80%, than those
18 reported previously for kimberlites from South Africa, Brazil and India, but overlap with PGE
19 results reported recently from Canadian kimberlites. Primitive-mantle-normalised chalcophile
20 element patterns are relatively flat from Os to Pt, but Cu, Ni and, somewhat less so, Au are enriched
21 relative to the PGE (e.g., Cu/Pd >25.000). Pd/Ir ratios are 3,6 on average, lower than most other
22 mantle melts. The PGE systematics can be largely explained by two components, (i) harzburgite /
23 lherzolite detritus of the SCLM with relatively high IPGE (Os-Ir-Ru) / PPGE (Rh-Pt-Pd) ratios, and
24 (ii) a melt component that has high PPGE/IPGE ratios. By using the concentrations of iridium in the

25 kimberlites as a proxy for the proportion of mantle detritus in the magma, we estimate that the
26 analysed kimberlites contain 3-27% entrained and partially dissolved detritus from the sub-
27 continental lithospheric mantle, consistent with previous estimates of kimberlites elsewhere (Tappe
28 S. et al., 2016, *Chem. Geol.* <http://dx.doi.org/10.1016/j.chemgeo.2016.08.019>). The other major
29 component in the samples is melt, modelled to contain an average of 0.85 ppb Pt and 1.09 ppb Pd.
30 Assuming that Group II kimberlites are derived from relatively metasomatised SCLM, our data
31 suggest that the metasomatised Karelian SCLM is relatively poor in Pt and Pd. If our data are
32 representative of other Group II kimberlites elsewhere, this result could imply that the PGE
33 enrichment in certain continental large igneous provinces, including Bushveld, is not derived from
34 melting of metasomatised SCLM.

35

36 **Keywords.** Kimberlite, platinum-group elements, sub-continental lithospheric mantle, Finland,
37 Karelian craton, Kaapvaal craton, Premier kimberlite pipe, Kaavi kimberlite

38

39 1. INTRODUCTION

40 Several recent workers have suggested that cratonic large igneous provinces (LIPs) are more
41 prospective to host deposits of platinum-group elements (PGE) than off-cratonic LIPs because
42 cratonic magmas can scavenge PGE during ascent through the sub-continental lithospheric mantle
43 (SCLM) (Zhang et al., 2008; Griffin et al., 2013; Hughes et al., 2015). However, the global
44 database on SCLM rocks, consisting largely of mantle xenoliths in kimberlite and basalt, indicates
45 that the cratonic SCLM is mostly relatively Pt and Pd depleted compared to the primitive mantle
46 (Irvine et al., 2003; Pearson et al. 2003, 2004; Wittig et al., 2010; Maier et al., 2012; Barnes et al.,
47 2015). It could be argued that the xenoliths are not representative of the PGE content of the SCLM
48 as the most metasomatised, potentially relatively PGE enriched, mantle components should be
49 relatively more susceptible to entrainment, disaggregation and dissolution during mantle melting

50 and magma ascent. In order to address the question whether the SCLM can be locally enriched in
51 PGE we determined the concentrations of PGE in 9 samples of kimberlite from the Karelian craton
52 and 2 samples from the Kaapvaal craton.

53 Kimberlites are volatile-rich, potassic, ultramafic igneous rocks that are the main hard-rock
54 source of diamond. They are normally sub-divided into Group I and Group II. Group I has
55 abundant large crystals of olivine, in a matrix of olivine, monticellite, perovskite, spinel, mica,
56 calcite, and serpentine, whereas Group II typically has abundant phlogopite ± olivine in a matrix of
57 phlogopite, K-richterite, and other diagnostic minerals. Mitchell (1995) reinstated the name
58 “Orangeites”, originally coined by Wagner (1928), for the Group II kimberlites. Mineralogically,
59 the orangeites are akin to olivine lamproites (except for the lack of carbonate in the latter), and it is
60 now generally agreed that orangeites are the southern African equivalents of lamproites (Mitchell,
61 2006), rather than being synonymous with Group II kimberlites in general.

62 Kimberlites are characterized by high abundances of not only the most incompatible trace
63 elements (e.g., Rb, Ba, Th, Nb, LREE, Sr), but also of compatible elements such as Mg, Ni and Cr.
64 This paradoxical duality is interpreted to reflect the mixing of incompatible element-rich kimberlite
65 ”melt” with MgO-, Ni- and Cr-rich lithospheric mantle rocks, the dissolved and undissolved
66 remnants of which form the rock and mineral detritus in kimberlites known as xenoliths,
67 macrocrysts and megacrysts. In view of the mostly relatively low Pt and Pd contents of sub-
68 continental lithospheric mantle harzburgite and lherzolite sampled by nodules and massifs (average
69 around 3-5 ppb Pt, <1-3 ppb Pd; Irvine et al., 2003; Pearson et al., 2004; Becker et al., 2006; Smith
70 et al., 2009; Wittig et al., 2010; Maier et al., 2012), it is likely that, if the SCLM contained more
71 PGE-rich portions, these were more fusible and may have formed from metasomatic melts or
72 fluids. As such, they could be represented by the kimberlites, notably those of Group II for which
73 SCLM derivation is least controversial (Mitchell, 2006). In contrast, if both kimberlites and SCLM
74 derived xenoliths are PGE depleted compared to the sub-lithospheric mantle, this would lend

75 further credence to the model that the SCLM in general is relatively PGE poor.

76

77 **2. SAMPLES**

78 The Karelian Group II samples analysed here are from the 1.2 Ga Seitäperä intrusion and the
79 Lentiira dike swarm located between the villages of Kuhmo and Lentiira in eastern Finland
80 (O'Brien and Tyni, 1999; O'Brien et al., 2007), 350 km inwards from the craton margin (**Fig. 1**). The
81 most distinctive feature of these potassic, ultramafic rocks is their phlogopite-rich nature (**Fig. 2a**).
82 Phlogopite occurs rarely as macrocrysts, but it is abundant as phenocrysts and microphenocrysts
83 with relatively Ti-rich compositions similar to those of microphenocrysts in lamproites. The more
84 primitive potassic rocks may also contain large amounts of olivine macrocrysts and, in some cases,
85 abundant xenocrysts and xenoliths of mantle peridotite. Additional groundmass minerals include K-
86 richterite, Mn-rich ilmenite, Cr-rich spinel zoned to Ti-magnetite, apatite and perovskite in a calcite
87 + serpentine matrix. More evolved versions of this rock type contain abundant olivine phenocrysts,
88 low-Al clinopyroxene, and phlogopite that is zoned to low-Ti tetraferriphlogopite, similar to mica
89 zoning trends in Group II kimberlites (Mitchell, 1995). Because the rocks contain primary
90 carbonate, they are more akin to South African Group II kimberlites (orangeites) than olivine
91 lamproites or ultramafic lamprophyres. Similarly to orangeites, the Seitäperä Group II kimberlites
92 have enriched Nd isotopic signatures with ϵ_{Nd} around -7, yet with distinct compositions of
93 $^{87}\text{Sr}/^{86}\text{Sr}_i$ around 0.704-0.706 (**Fig. 3**; Kargin et al., 2013; O'Brien, 2015).

94 The Finnish Group I kimberlite samples come from the 600 Ma old pipes of the Kaavi-Kuopio
95 kimberlite clusters that are located in a craton margin tectonic setting in eastern Finland. Samples of
96 pipes 1,2,3,5,9,10, and 14 are hypabyssal kimberlites. They all have typical Group I mineralogies
97 (i.e. abundant large rounded grains (macrocrysts) of olivine in a matrix of subhedral to euhedral
98 olivine, monticellite, perovskite, spinel, mica, apatite, calcite and serpentine), major and trace
99 element and isotopic compositions (O'Brien and Tyni, 1999). They display the classic suite of

100 lithospheric mantle-derived xenoliths and xenocrysts (**Fig. 2b**), including (i) variable amounts of
101 olivine showing a trimodal size distribution with abundant 0.1-0.4mm size grains mostly interpreted
102 as phenocrysts, 1-5 mm sized rounded macrocrysts, and occasional cm sized megacrysts. (ii) Mg-
103 ilmenite, (iii) pyrope garnet derived from a range of sources including high Cr, Ca-depleted
104 harzburgite to Ca-saturated lherzolite and Ca-rich wehrlite, to Ti-rich megacryst-compositions, and
105 orange garnets derived from mantle eclogite, (iv) clinopyroxene comprising lherzolitic, low-Cr
106 megacrystic, and eclogitic subgroups (O'Brien, 2015), and (v) spinels from upper mantle spinel
107 lherzolites and rare chromites plotting within the diamond inclusion field (O'Brien, 2015). The
108 rocks have relatively depleted isotopic signatures (Kargin et al., 2014) plotting close to South
109 African Group I kimberlites as well as kimberlites in Canada (Tappe et al., 2016) in ϵ_{Nd} vs Sr_i ,
110 albeit at slightly lower ϵ_{Nd} (around 0) (**Fig. 3**, O'Brien and Tyni, 1999).

111 In addition to the Finnish kimberlites, we also analysed two kimberlite samples from the
112 Kaapvaal craton. They represent Group I hypabyssal tuffissitic kimberlite breccias exposed in drill
113 core from the 1151 Ma (Wu et al., 2013) Premier pipe, located in the vicinity of Pretoria. The rocks
114 contain abundant large (up to 1 cm in diameter) macrocrysts and clasts of pelitic and quartzitic
115 country rocks set in a fine grained groundmass. The lithophile element composition of the rocks has
116 previously been reported in Maier et al. (2005), and geological-mineralogical data on the Premier
117 pipe can be found in Bartlett et al. (1994) and de Wit et al. (2016).

118

119 **3. ANALYTICAL METHODS**

120 All of our samples have been characterised for major and trace elements at the Geological Survey of
121 Finland in Espoo. The concentration of the lithophile elements in the Finnish samples is reported in
122 O'Brien and Tyni (1999) and that of the Premier samples in Maier et al. (2005). Preparation of the
123 Finnish kimberlite samples involved crushing of approximately 500 g of sample material into small
124 chips with a hammer and hand-picking approximately 200 g of chips least contaminated by crustal

125 xenoliths. No attempt was made to separate mantle xenoliths from kimberlite. The hand-picked
126 material was powdered in a steel grinding vessel. Major elements and S were determined by XRF
127 on fusion beads, H₂O and CO₂ by LECO analyzer, Ba, Ni, Cr, Cu, Zn, Sr and Zr by XRF on pressed
128 pellets and REE, Hf, Ta, Pb, Th, U, Nb, Y, Rb, Sc, V, and Co by ICP-MS. Analytical methods are
129 reported in O'Brien and Tyni (1999) and the data are provided in **Table 1**.

130 The PGE (Os, Ir, Ru, Rh, Pt, Pd) and Au have previously been determined by Ni-fire assay Te-
131 co-precipitation followed by ICP-MS at the Geological Survey of Finland. Details of the analytical
132 method are outlined in Juvonen et al. (2002) and the data are listed in **Electronic Appendix 1**. The
133 concentration of Pt and Pd in the kimberlites were found to be very low (mostly <2 ppb) and lower
134 than those reported in the literature for kimberlites (McDonald et al., 1995). In order to obtain better
135 precision the samples were additionally analysed by high pressure asher digestion followed by
136 online separation and quantification by isotope-dilution (HPA-ID) using ICP-MS following the
137 method of Meisel et al. (2003). Rock powder (2 g) was weighed in a 30 ml quartz HPA tube. Five
138 milliliters of 15 mol l⁻¹ HNO₃ and 2 ml of 12 mol l⁻¹ HCl (both environmental grade) were added
139 and variable amounts of a PGE-mixture spiked solution (UQAC-S-1) were added. The quartz lids
140 were closed with a quartz disk and a PTFE (polytetrafluoroethylene) strip prior to high-pressure
141 digestion at 300°C for 4.5 hr. The confining pressure was adjusted to 100 bars at the beginning and
142 increased to 130 bars during digestion. After digestion, the samples were transferred to a 30 ml PFA
143 container and directly sparged into the ICP-MS by bubbling argon through the sample for osmium
144 isotope ratio determination. The samples were dried at 70–80 °C and the residuum was diluted with
145 2-10 ml of 0.1 mol l⁻¹ HCl. After centrifugation, 1 ml of the solution was introduced into a 1-m-long
146 cation exchanged resin column (previously washed with 6 mol l⁻¹ HCl and equilibrated at 0.1 mol l⁻¹
147 HCl). The column was directly attached to the ICP-MS for 'online' separation. A multiple PGE-Au
148 and Re stock solution (SCP Science, Canada) was used to monitor the mass drift. The enriched

149 isotopes in the spike mixture are ^{99}Ru , ^{108}Pd , ^{185}Re , ^{190}Os , ^{191}Ir and ^{198}Pt while the isotopes used for
150 quantification are ^{101}Ru , ^{106}Pd , ^{187}Re , ^{188}Os , ^{193}Ir and ^{196}Pt . Because they are monoisotopic, Rh and
151 Au cannot be determined by isotope dilution technique. The signal detected from the acid blank (0.1
152 mol l⁻¹ HCl) injected in the column prior to each analysis was subtracted from the raw count to the
153 detector. When counts are present in the blank, the blank/sample proportion is far less than 1%.
154 Because the on-line separation leads to changes in the signal intensity with time, it is difficult to
155 convert the blank signal into an equivalent concentration, thus limits of detection can only be
156 estimated and are ranging between 0.003-0.086 ng g⁻¹ for Re and Pd, respectively (Savard et al.,
157 2010). Indeed, as it is stated in Savard et al. (2010): “The MLD cannot readily be calculated
158 precisely for HPA-ID because the result is obtained by a summation of the signal integrated over a
159 period of time that can vary, and during which the signal intensity also varies”. As also stressed in
160 Meisel et al. (2003), the technique requires only concentrated acids and highly diluted HCl, thus
161 procedural blank levels are controlled by the quality of the acid. Meisel et al. (2003) presented
162 detection limits calculated on the absolute amount of total procedural blanks using reagent grade
163 acids and found total procedural blanks ranging between 4 pg and 408 pg for Os and Pt,
164 respectively. For the present work, the environmental acid grade used, in combination with a newer
165 generation of ICP-MS instrument (Agilent 7700X) resulted in absolute procedural blanks ranging
166 between 0.4 pg and 9.3 pg for Re and Pt, respectively (see **Table 2**). These values are lower than the
167 detection limit (**Table 3**). More details on the method are provided in Meisel et al. (2003), Savard et
168 al. (2010), Meisel and Moser (2004a, b) and Savard et al. (2010).

169 Table 3 reports results obtained for the reference materials analyzed together with the kimberlite
170 samples to monitor quality. Results for OKUM agree with certificate values within the confidence
171 limits. For Re and Os there are no certificate values, therefore the values obtained by Savard et al.
172 (2010) are listed for comparison. The results for Re are similar, however the Os value is
173 considerably higher, at 1.2 ng/g vs 0.79 ng g⁻¹. It is possible that the difference in Os values is real,

174 and due to inhomogeneity in the sample, given the low concentration of Os and the low sample
175 weight used in isotope dilution. A round robin has recently been conducted on PGEs, Re and Au in
176 OKUM in order to obtain certification of OKUM following ISO guidelines (Kane and Potts, 1997),
177 however the report is not yet available (Thomas Meisel, personal communication). From 8
178 participating laboratories who provided Os concentrations using various preparation and analytical
179 techniques (fire assay, Carius tube, isotope dilution, acid digestion, fusion, Q-ICP-MS, MC-ICP-
180 MS), the data range from ~0.4 to ~1.6 ng g⁻¹ Os, with >20% of the provided results showing values
181 >1 ng g⁻¹ Os. It was suggested that the working value for Os in OKUM after “outlier rejection”
182 should be 0.85 +/- 0.12 ng g⁻¹ Os, thus RSD is ~14% suggesting Os distribution in OKUM is
183 inhomogeneous (Thomas Meisel, personal communication). In the present work, two aliquots of
184 OKUM were analyzed and the relative standard deviations for Ru, Pd and Pt are < 5%. However for
185 Os, Ir and Re the relative standard deviations are higher, ranging between 15% and 21% RSD. The
186 higher relative standard deviations for these elements may be the result of a combination of low
187 sample weights, low concentrations and inhomogeneous distribution of the elements in the sample.
188 Again, results from the round robin show that RSD for Ir, Ru, Pt are around 12-13%.

189

190 **4. RESULTS**

191 The results for PGE by HPA-ID-ICP-MS analyses cover a similar range to those obtained by
192 Ni-fire assay (**Fig. 4**). Combined Pt + Pd contents of the analysed Group I and Group II kimberlites
193 from Finland and South Africa are generally below 5 ppb (**Table 2**). On average, the samples
194 contain 1.38 ppb Pt and 1.33 ppb Pd (Pt/Pd ~1). There is very little difference between Group I and
195 Group II, except that average Au contents of Group II samples are about twice those in Group I
196 (1.19 ppb vs 0.63 ppb, respectively). There is also little difference in PGE contents between the
197 Premier samples and the other kimberlites, a surprising result in view of the fact that Premier
198 intruded rocks of the Bushveld Complex, the world’s largest repository of PGE. Combined IPGE

199 contents in our kimberlite samples are between ~1 and ~4 ppb, with average values being 0.77 ppb
200 Os, 0.51 ppb Ir, 1.22 ppb Ru, and 0.34 ppb Rh.

201 Most of the mantle normalised PGE patterns are moderately fractionated ($\text{Ir/Os} = 0.71 \cdot \text{CI}$,
202 $\text{Ir/Ru} = 0.64 \cdot \text{CI}$, $\text{Ir/Rh} = 0.42 \cdot \text{CI}$) (CI from McDonough and Sun, 1995), but $\text{Pd/Ir} = 2.18 \cdot \text{CI}$ and Pt/Ir
203 $= 1.23 \cdot \text{CI}$ (Table 2). The Pd/Ir ratios are lower, and the metal patterns less fractionated, than in most
204 other mantle derived magmas, with the exception of some komatiites and picrites (see compilations
205 in Barnes et al., 1985; Maier and Barnes, 2004; Fiorentini et al. 2010; Day et al., 2013; Barnes et
206 al., 2015). However, the metal patterns mostly show enrichment in Ni, Cu and Au relative to PGE
207 on mantle normalized plots (**Fig. 4a-c**).

208 Our samples show markedly lower PGE contents than the kimberlites analysed by
209 McDonald et al. (1995) who reported average concentrations of 1.45 ppb Os, 1.34 ppb Ir, 2.97 ppb
210 Ru, 0.9 ppb Rh, 7.7 ppb Pt, 5.1 ppb Pd and 1.8 ppb Au in their Group I and Group II samples from
211 South Africa and Brazil (**Fig. 4e-f**). Our PGE contents are also lower, by about 50%, than the results
212 of Rao et al. (2014) for orangeites from the Bastar craton of India which showed average PGE
213 contents of 3.5 ppb Ru, and ~3 ppb Pt and Pd each (Fig. 4g) However, our PGE levels are broadly
214 similar to those of Tappe et al. (2016) who analysed Os, Ir, Ru, Pt, Pd and Re in two Canadian
215 kimberlite clusters (Renard and Wemindji), using ID-N-TIMS for Os and ID- ICP-MS for the other
216 PGE (**Fig. 4h**). It is thus possible that kimberlites have more variable PGE contents than reported
217 by us. Alternatively, the relatively high PGE levels in the study of McDonald et al. (1995) could
218 reflect the lower precision of the INAA method and the heterogeneity of the standard used; Tredoux
219 and McDonald (1996) state coefficients of variation between 10 and 20% for the analysis of Pt and
220 Pd in standard WITS-1 used by McDonald et al. (1995). Future work will undoubtedly clarify this
221 issue.

222

223 **5. DISCUSSION**

224 **5.1. Petrogenesis of platinum-group elements in kimberlites**

225 The estimated concentrations of the PGE in the Earth's primitive mantle (PM) range from 1-7 ppb
226 for individual elements (Palme and O'Neill, 2003; Barnes and Maier, 1999, Puchtel et al., 2004,
227 Becker et al., 2006; Fischer-Gödde et al., 2011; Aulbach et al., 2016). Metal patterns in SCLM
228 xenoliths show broadly similar levels on mantle normalized plots for Ni and the IPGE (Os, Ir, and
229 Ru) at around 1 times primitive mantle, but Pt, Pd, Au and Cu tend to be variably depleted relative
230 to the IPGE and PM (Pearson et al., 2003, 2004). This pattern is generally interpreted to be the
231 result of extraction of basalt and komatiite from PM, with Ni and the IPGE behaving compatibly
232 during much of the melting history due to partitioning into chromite, olivine, sulfides and alloys,
233 whereas Pt, Pd, Au and Cu are incompatible (Barnes et al., 1985; Peach et al. 1990; Fleet et al.
234 1991, 1999; Sattari et al. 2002; Lorand et al., 2013; Mungall and Brenan, 2014; Aulbach et al.,
235 2016; Brenan et al. 2016). Current estimates of the average PGE content of the SCLM suggest
236 about 50-70% less Pt and Pd than in PM (Irvine et al., 2003; Pearson et al., 2004; Maier et al.,
237 2012), but there is a certain degree of regional variation, with some cratons being relatively
238 depleted compared to the global average (Greenland, Wittig et al., 2010) whereas others are slightly
239 enriched (see compilation of data for various cratons in Maier et al., 2012). Rhodium behaves in a
240 transitional manner, as seen by its relatively slight depletion relative to IPGE in the xenolith data
241 (Fischer-Gödde et al., 2011; Maier et al., 2012; Barnes et al., 2015).

242 Assuming an average concentration of 250 ppm S in the convecting mantle (approximately
243 0.06% sulfide; McDonough and Sun, 2005), and a S solubility in basalt - komatiite at sub-
244 lithospheric depth (>100-150 km) on the order of 500-1000 ppm (Mavrogenes and O'Neill, 1999),
245 the bulk of the mantle sulfide is normally considered to be dissolved during moderate to large
246 degree mantle melting (> 15-25%; Barnes et al., 1985; Mungall and Brenan, 2014). At lower
247 degrees of melting, sulfide would be incompletely dissolved and thus the bulk of the highly
248 chalcophile Pt, Pd, Au and Cu may remain in the mantle. The Pt and Pd depletion observed in the

249 mantle normalized patterns of mantle xenoliths therefore implies that the bulk of the SCLM is the
250 residue of relatively large degree partial melting. Ballhaus et al. (2006) suggested that mantle
251 sulfides can be entrained in magmas that formed at small degrees of mantle melting, but based on
252 the low PGE contents reported here this model does not appear to apply to the kimberlites discussed
253 in the present paper.

254 As few mantle SCLM xenoliths contain less than 1 ppb Pd, the SCLM appears to have been
255 refertilized with melt or fluid that contained some Pd (Lorand et al., 2008; 2013), and this probably
256 also introduced some Cu, Pt and Au. The precise nature and PGE content of the refertilising agent
257 remains debated and was likely diverse (Simon et al., 2007; Kamenetsky et al., 2013), but the
258 paucity of mantle samples that contain significantly higher Pt and Pd than PM (Pearson et al., 2004;
259 Maier et al., 2012; Lorand et al., 2013) suggests that the agent was relatively PGE poor (but see
260 Hughes et al. 2014 and Marchesi et al. 2014 for examples of relatively PGE rich SCLM xenoliths
261 from the North Atlantic craton and the Rhonda peridotite massif).

262 Compared to most other mantle derived magmas (Fiorentini et al., 2010; Barnes et al., 2015)
263 the kimberlites analysed in the present study have relatively unfractionated PGE patterns (but with
264 several samples showing positive Rh anomalies) that can be modeled as a mixture of PGE-poor
265 melt with high PPGE/IPGE ratios, and SCLM detritus (**Fig. 4**). For example, a 20% component of
266 average SCLM (Maier et al., 2012) would result in ~ 0.7 ppb Ir, 0.8 ppb Pt, and 0.4 ppb Pd,
267 accounting for most of the Ir in the analysed kimberlites, but only a fraction of the Pt and Pd. We
268 can broadly replicate the measured patterns of the kimberlites, including the unique positive Rh
269 anomalies, with a mixture of 10-20% average Kaapvaal peridotite xenoliths and 80-90% melt
270 represented by the “liquid” component (see section 5.4 and **Electronic Appendix 2** for calculation
271 method) of MARID xenoliths, rocks that are composed mainly of mica, amphibole, rutile, ilmenite,
272 and diopside (Dawson and Smith, 1977). The MARIDs have been interpreted, by some authors, as
273 mixtures between SCLM derived melts and mantle peridotite (Waters, 1987; Gregoire et al., 2002).

274 They contain, on average, 2.4 ppb Pt and Pd each, and have more fractionated PGE patterns than
275 the harzburgite xenoliths, with Pd/Ir ~11 and Cu/Pd ~26000 (Maier et al., 2012). It should be noted
276 that in addition to peridotite and MARID melt, the elevated CO₂ contents of kimberlite requires a
277 carbonate component, possibly derived from melting of trace carbonatite in the SCLM.

278 The similarity in PGE patterns between Group I and Group II kimberlites seen in figure 4 is
279 notable, being that most authors interpret the 2 types of kimberlites to be derived from different
280 mantle sources; Group I kimberlites have Nd and Sr isotope ratios around CHUR, putatively
281 reflecting an asthenospheric source (e.g., Tappe et al., 2012), whereas Group II kimberlites have
282 strongly radiogenic Sr and unradiogenic Nd isotopes, arguably reflecting a lithospheric mantle
283 dominated source (Smith, 1983; Tainton and McKenzie, 1994; Mitchell, 2006; O'Brien, 2015). One
284 might expect that melts from such diverse mantle domains should have contrasting PGE patterns.

285 We suggest that the similarity in PGE patterns can be understood within the context of a
286 model whereby the bulk of the PGEs in both types of kimberlite is derived from refractory cratonic
287 mantle material. The metasomatised component of the SCLM was PGE poor, consistent with the
288 low sulfide and PGE contents of MARIDs and other metasomatised harzburgite/lherzolite xenoliths
289 (Pearson et al., 2004; Maier et al., 2012; Lorand et al., 2013). Only Group II magmas fused potassic
290 metasomes that control the lithophile trace element isotope systems such as Rb-Sr, Sm-Nd, Lu-Hf,
291 thereby causing the enriched isotope signatures of the Group II magmas. In both the Karelian and
292 Kaapvaal craton the Group II kimberlites are older than the Group I kimberlites; Possibly, Group I
293 kimberlites retained their relatively depleted isotopic signature during traverse through the SCLM
294 because the SCLM had become relatively refractory, following melting events that may have
295 included the one which resulted in the Group I kimberlites.

296 We considered whether the PGE could have been extracted from the kimberlites by sulfide
297 or sulfate that segregated during magma ascent and contamination in the crust. The kimberlites have
298 variable amounts of lower, middle and upper crustal material, but none of these rocks contain

299 significant sulfur. In any case, kimberlite magmas are generally believed to ascend relatively fast
300 within the crust, as suggested by the abundance of dense phases such as spinel crystals and large
301 peridotite fragments, and by the presence of diamonds which would have been amenable to burning
302 if the magma ponded or decelerated. This suggests that the ubiquitous PGE depletion of the
303 kimberlites was not caused by the segregation of small sulfide droplets from the magmas.

304

305 **5.2. Implications for the genesis of Bushveld Complex magmas**

306 The Bushveld Complex is the largest layered intrusion on Earth. The extensive granitic, rhyolitic
307 and mafic-ultramafic rocks outcropping across $> 100\,000\text{ km}^2$ of southern Africa are the result of
308 one of the world's largest igneous events, with $> 1\text{M km}^3$ of magma (Rajesh et al., 2013). The
309 Complex has been interpreted as having crystallised from melts derived, at least in part, from the
310 SCLM, based on Os isotopes and high Pt/Pd ratios of 1.6 that mirror, amongst known mantle
311 reservoirs, only the SCLM (Maier and Barnes, 2004; Richardson and Shirey 2008, Barnes et al.,
312 2010). However, if our kimberlite data are representative of not just the Karelian craton, but also the
313 Kaapvaal craton, as suggested by the similarity in PGE patterns between the Karelian and Premier
314 kimberlite samples, this interpretation seems difficult to reconcile with the low PPGE contents and
315 the unfractionated PGE patterns in our samples, implying low PGE contents of the metasomatic
316 component of the SCLM, as discussed above; Bushveld melts have not only much more
317 fractionated PGE patterns than kimberlites (**Fig. 5**), but amongst the highest PGE contents of global
318 magmas, and they also lack the positive Au anomalies observed in Group II kimberlites (**Fig. 5**).
319 Furthermore, MELTS modelling indicates that partial melting of fertile SCLM at 30 kbar yields
320 magma that has significantly lower SiO_2 and CaO, and far higher incompatible lithophile trace
321 element contents than unevolved Bushveld B1 magma (Maier et al., 2016). We thus conclude that,
322 if the PGE contents of the two analysed Premier kimberlites are representative of other Kaapvaal
323 kimberlites, the PGE-rich Bushveld magmas are unlikely to be derived mainly from the

324 metasomatised portion of the SCLM. Alternatively, it is possible that the PGE contents of our
325 Premier kimberlite samples are not representative of Kaapvaal kimberlites, as potentially suggested
326 by the data of McDonald et al. (1995). However, as pointed out earlier, we feel that the INAA
327 method used by these authors lacks the precision required to reliably determine the low abundances
328 of PGE in kimberlites. Future studies will doubtlessly shed more light on this issue.

329 A further possibility is that the SCLM xenoliths so far analysed from the Kaapvaal craton
330 are non-representative. Marchesi et al. (2014) and Hughes et al. (2014) have reported elevated PGE
331 contents (and high Pt/Pd > 1) in the Rhonda SCLM massif and in xenoliths from the North Atlantic
332 craton. One could thus argue that the Kaapvaal SCLM too contains domains that are more enriched
333 in PGE than those samples by the xenoliths analysed so far, and that Bushveld magmas selectively
334 scavenged PGE from the ~ 150 km thick refractory SCLM during ascent. Additional work on the
335 Kaapvaal mantle rocks is required to resolve this issue. .

336

337 **5.3. Origin of elevated Au contents in the Group II kimberlites**

338 The positive Au anomalies and elevated Au contents of the Group II samples relative to Group I
339 kimberlites could suggest that the metasomatised component of the SCLM is relatively enriched in
340 Au. This observation is potentially consistent with studies suggesting that the Au in orogenic Au
341 deposits is derived from alkaline magmas sourced from the lithospheric mantle (Hronsky et al.,
342 2012). However, due to the small number of Group II samples analysed by us this model remains
343 highly speculative and needs to be tested by analysis of further samples. Notably, a relative Au
344 enrichment was also observed in South African orangeites relative to South African Group I
345 kimberlites by McDonald et al. (1991).

346

347 **5.4. Estimating the proportion of xenoliths, xenocrysts and primary kimberlite melt**

348 Kimberlites contain abundant xenoliths and xenocrysts in various states of dissolution. This

349 is, for example, reflected in trajectories from kimberlite towards the lithospheric mantle data array in
350 binary Ir vs Ru and , to a lesser degree, Ir vs MgO diagrams (**Fig. 6**). Previous authors have
351 attempted to quantify the relative proportion of peridotite detritus and kimberlite liquid by using a
352 variety of modelling approaches, including subtraction of olivine or peridotite from bulk kimberlite
353 (Fraser and Hawkesworth, 1992; Le Roex et al., 2003; Kjarsgaard et al., 2009), mixing models of
354 Os isotope ratios (Pearson et al., 2003; Tappe et al., 2016), Nd-Hf isotopes (Tappe et al., 2013),
355 calculating melt composition from the composition of non-xenocrystic olivine (Arndt et al., 2010),
356 analysis of quenched kimberlite melt (Price et al., 2000; Kopylova et al., 2007), and melt inclusions
357 in olivine (Kamenetsky et al., 2013). With the exception of the melt inclusion work that yielded
358 highly carbonaceous melt estimates, most of the proposed melt compositions show relatively good
359 consistency (e.g., 20-30% SiO₂ and MgO, 1300-2400 ppm Cr, 800-1400 ppm Ni).

360 A potential shortcoming of the olivine-peridotite subtraction method is that kimberlites have
361 MgO, Cr and Ni contents that differ by a factor of less than 2 from the composition of lithospheric
362 mantle peridotites, rendering these elements relatively insensitive tracers of melt-peridotite mixing
363 (Smith et al., 1985; Shee, 1986; Taylor et al., 1994; Berg and Carlson, 1998; Price et al., 2000, Le
364 Roux et al. 2003, Harris et al., 2004, Becker and Le Roex, 2006).

365 In the present paper, we estimate the proportion of detrital material in kimberlite by using
366 mass balance based on Ir contents. The reasoning behind this method is that Ir abundances in low-
367 degree mantle melts and lithospheric peridotites show very different concentrations, and that Ir is
368 mostly relatively immobile during mantle metasomatism and near surface alteration (but see
369 Ackerman et al., 2009, and Lorand et al., 2013, for examples of Ir depleted metasomatised mantle
370 rocks). Iridium was also chosen for more practical reasons: due to low reagent blanks and a lack of
371 interfering ions it can be accurately determined not only by ID but also by conventional analytical
372 techniques such as nickel sulfide fire assay followed by ICP-MS finish.

373

374 The following equations apply:

375 (1)
$$Ci(pk_m) = \frac{[CIr(s) - f(a) \times Ci(a)]}{[1 - f(a)]}$$

376

377 (2)
$$f(a) = \frac{[CIr(s) - CIr(pk_m)]}{[CIr(a) - CIr(pk_m)]}$$

378 where Ci and CIr refer to the concentrations of an element of interest and iridium in the sample (s),
379 the lithospheric mantle assimilant (a), and the primary kimberlite magma (pk_m). $f(a)$ refers to the
380 volume fraction of the assimilant in the sample. To solve the equation for unknown elements one
381 needs to know the composition of the assimilant and the Ir content of the primary kimberlite melt.

382 The composition of the assimilant is estimated by averaging the compositions of mantle
383 xenoliths that have been recovered from kimberlite pipes. With the exception of a few pipes
384 (notably Jagersfontein), this proved to be remarkably homogenous for the Kaapvaal and Karelian
385 cratons, at 3.67 ppb Ir for the Kaapvaal craton (n=83, stdev 1.62ppb) and 3.62 ppb Ir for the
386 Karelian craton (n=18; stdev 2.19, Pearson et al., 2004, Becker et al., 2006; Maier et al., 2012).
387 Alard et al. (2000) have proposed that in cratonic peridotites Ir is mainly bound in sulfide minerals
388 found as inclusions in olivine, but Luguét et al. (2007) showed that in the Lherz massif laurite
389 inclusions may occur in addition to Pt-Ir-Os alloys. Although the Ir content of kimberlite thus
390 basically is a measure of the amount of sulfide and alloy contamination, it is likely that kimberlite
391 melt has assimilated bulk mantle peridotite, rather than selectively Ir-rich mineral phases; The latter
392 are protected from selectively dissolving into kimberlite magma by the enclosing olivine crystals
393 (macrocrystal olivine) which show only minor reaction with the melt. Because the Ir content of
394 kimberlite melt is low (see below) and $D_{Ir}(ol-melt)$ is only around 2 (e.g., Brenan et al., 2005),
395 possible removal of some phenocrystic olivine has no significant effect on the iridium content of the
396 melt. Furthermore, a case can be made against gravitational removal of macrocrystal olivine ($\rho=3.3$

397 g/cm³), because kimberlites contain abundant picroilmenite, garnet, and diamond xenocrysts, all of
398 which have higher densities than olivine. Although nugget effect is always a possibility, we are
399 confident that the extensive degree of assimilation by the rigorously mixing kimberlite magma
400 provides us with well homogenised kimberlite samples in which Ir can be applied as a proxy for the
401 degree of mantle assimilation.

402 The Ir content of the kimberlite parental magma can be estimated from general mantle melting
403 constraints and the Ir content of other alkaline magma types; Firstly, Ir is largely bound in mantle
404 sulfides (Alard et al., 2000) and, to a lesser degree, in olivine (Brenan et al., 2005). Partition
405 coefficients between sulfide and silicate melt are between 10^5 and 10^7 (Fonseca et al., 2009;
406 Mungall and Brenan, 2014), and between olivine and silicate melt are ~ 2 (Brenan et al., 2005). As a
407 result, batch melting calculations yield <0.05 ppb Ir in melts with $F < 5\%$. Secondly, the available
408 literature data indicate that most alkaline basalts have very low iridium contents (Vogel and Keays,
409 1997; Rehkämper et al., 1999; Tatsumi et al., 2000; Crocket et al., 2002; Barnes et al., 2015).
410 Concentrations range from 0.002 to 0.365 ppb with a median value of 0.06 ppb (n=33). From these
411 estimates we conclude that it is unlikely that primary kimberlite melts contain significantly more
412 than 0.05 ppb iridium.

413 Calculations using Equation (2) suggest that the volume percentage of the lithospheric mantle
414 material in Finnish Group I and II kimberlites is between 3-22 wt.%. The two Premier samples
415 analysed have 18-27% mantle detritus. These estimates overlap with those of Tappe et al. (2016) for
416 Canadian kimberlites (2-30%).

417 Equation (1) cannot be readily applied to calculate primary major and lithophile trace element
418 “melt” compositions for our samples. This is because for major and lithophile trace elements,
419 potential uncertainties are much larger than in the case of PGE, as the compositional difference
420 between the contaminant (the xenoliths) and the kimberlite melt is far smaller than for PGE, and
421 accumulation and fractionation effects are potentially far more significant; For example, a small

422 amount of cumulus phlogopite in the kimberlites dramatically changes the K and Rb contents of the
423 rock.

424

425 **6. CONCLUSIONS**

426 (i) The present study presents high-precision isotope dilution data for Os, Ir, Ru, Pt, and Pd in
427 kimberlites. Platinum and Pd contents of the rocks are generally very low (averaging around
428 1.3-1.4 ppb Pt and Pd each, 2-3 ppb combined IPGE), in contrast with some previous studies
429 that proposed up to 4-7 times higher Pt and Pd contents and 2-3 times higher IPGE contents.
430 We propose that the differences are largely due to the inferior precision and accuracy of those
431 previous studies conducted by using INAA. In contrast, previous studies using ICP-MS (Tappe
432 et al., 2016) have obtained PGE levels broadly overlapping with our results.

433 (ii) The PGE patterns of the kimberlites can be interpreted to represent mixtures of PGE poor melt
434 and variably dissolved SCLM xenoliths and xenocrysts. Using Ir as a proxy, we have estimated
435 the proportion of mantle detritus in the kimberlites to be between 3 and 28%.

436 (iii) Our data from the Karelian craton and the Premier pipe in South Africa suggest that the
437 metasomatised component of the SCLM is relatively PGE poor. If the 2 Premier samples are
438 representative of the Kaapvaal craton, this would imply that the high PGE contents and Pt/Pd
439 ratios in Bushveld magmas are not derived from melting of the metasomatised Kaapvaal
440 SCLM, and that the prospectivity of LIPs is not controlled by the interaction of the magmas
441 with cratonic SCLM, as proposed in some recent studies.

442 (iv) The Group II kimberlites have positive Au anomalies in mantle normalised diagrams suggesting
443 that the metasomatic component of the SCLM is relatively enriched in Au compared to PGE,
444 and that the metasomatised SCLM could have supplied noble metals for orogenic Au deposits
445 (Hronsky et al., 2012; Griffin et al., 2013).

446

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448

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451

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702

703 **Figure Captions**

704

705 Fig. 1: Simplified geological map, showing locality of Finnish kimberlites analysed. Figure
706 modified after Peltonen and Brüggemann, (2006).

707

708 Fig. 2 (a) Phlogopite-rich group II kimberlite from dyke 16, Lentiira. Pool of late stage liquid in
709 centre of photomicrograph is surrounded by phlogopite, tetraferriphlogopite, diopside, K-richterite.
710 On right side of section are olivine pseudomorphs rimmed by perovskite. Plane polarised light.
711 Modified after O'Brien and Tyni, 1995. (b) Thin section of hypabyssal kimberlite from Pipe 9 with
712 abundant macro- and phenocrysts of olivine, as well as a fresh garnet lherzolite xenolith, containing
713 olivine, orthopyroxene, red to purple pyrope, gray Mg-ilmenite, and bright green Cr-diopside. Plane
714 polarized light. (c) Backscattered electron image of a Pipe 1 sample from Kaavi, Finland. Rounded
715 olivine (bright green) is mostly altered in this sample, and all cases has a necklace of monticellite
716 (red). Oxides are chromites (euhedral white) or late MUM spinel (skeletal small crystals, white to
717 light yellow). Matrix is composed of serpentine (dk green), calcite (brown), kinoshitalite mica
718 blades (yellow-orange) and euhedral apatite crystals (dark orange).

719

720 Fig. 3: Nd and Sr isotopic characteristics of Finnish kimberlites, compared to kimberlites and other
721 alkaline rocks globally (modified after O'Brien, 2015). Data for Superior kimberlites are from

722 Tappe et al. (2016)

723

724 Fig. 4. PGE patterns of kimberlites, normalized to primitive mantle (normalization factors from
725 Becker et al. (2005) and Day et al. 2016). Data is best modelled by mixing of 10-20% SCLM and
726 80-90% MARID. Note that MARID data are normalised to mantle detritus-free composition, as
727 outlined in chapter 5.3.

728

729 Fig. 5: PGE patterns of Bushveld B1 sills (data from Barnes et al., 2010). Patterns of Premier
730 kimberlites (ID and Ni-sulfide analyses) shown in grey. Normalization factors from Becker et al.
731 (2005) and Day et al. (2016).

732

733 Fig. 6: Binary variation diagrams comparing composition of analysed kimberlites with Kaapvaal
734 and Karelian mantle xenoliths. Also plotted are diamond-bearing (Renard) and barren kimberlites
735 (Wemindji) from the Superior craton, Canada (Tappe et al., 2016). (A) Ru vs Ir, (B) MgO vs Ir.
736 Most Karelian and Kaapvaal kimberlites plot near tielines between probable kimberlite melt and
737 average Karelian SCLM (from Maier et al., 2012), suggesting that the main contaminant is garnet
738 peridotite. In contrast, Superior kimberlites are more MgO rich, possibly suggesting more dunitic
739 SCLM contaminants. Estimate of kimberlite melt is based on Price et al. (2000).

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Table 1: Whole rock data for Karelian and Kaapvaal kimberlites

Sample	KAI										
	D21	16-002	16-002	9729	9729	9729	9729	9729	9729	P10	P11
		26.95	23.83	5621	5611	5596	5603	5599	5604		
Craton	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Kaapvaal	Kaapvaal
craton											
loc	margin	margin	margin	margin	margin	margin	margin	margin	margin	centre	centre

pipe/dyke		d 16	d 16	p 10	p 14	p 2	p 5	p 3	p 9	Premier	Premier
Group	II	II	II	I	I	I	I	I	I	I	I
SiO ₂ (wt%)	23.44	42.95	36.07	35.28	34.96	32.08	35.99	29.69	39.43	39.81	37.72
TiO ₂	1.99	3.24	2.41	2.39	2.84	2.34	1.31	2.29	1.95	1.96	2.00
Al ₂ O ₃	3.14	4.01	2.30	5.02	3.48	5.43	2.74	4.88	3.62	2.11	2.46
Fe ₂ O ₃	7.97	9.93	9.79	9.59	11.49	11.79	9.47	11.29	9.32	9.36	9.63
MnO	0.28	0.14	0.15	0.19	0.19	0.26	0.17	0.35	0.15	0.14	0.15
MgO	15.02	21.68	29.47	24.19	29.96	22.58	28.39	20.89	26.95	27.31	27.06
CaO	22.48	5.44	4.87	8.30	3.78	10.09	7.27	12.59	6.19	7.16	8.24
Na ₂ O	dl	0.40	dl	0.21	0.14	0.10	0.14	0.11	1.05	0.06	0.01
K ₂ O	0.76	5.73	2.31	1.57	2.27	1.95	0.31	0.63	2.44	1.04	1.07
P ₂ O ₅	0.87	0.12	0.39	0.58	0.34	0.60	0.27	0.69	0.34	0.33	0.42
H ₂ O ⁺	na	na	na	10.14	9.68	8.96	10.50	10.50	9.36	na	na
LOI	na	na	na	na	na	na	na	na	na	8.96	9.43
C	na	na	na	0.74	0.47	1.01	1.27	1.90	0.10	na	na
Total	75.95	93.64	87.76	98.20	99.60	97.19	97.83	95.81	100.90	98.24	98.19
Zr (ppm)	217	319	149	103	63.7	94.4	52.8	96.6	69.1	80	80
Sr	1183	467	681	776	457	890	477	889	484	441	532
Co	na	80.8	85.7	62.8	78.2	59.9	80.5	52.7	67.8	88	84
Cr	750	1238	905	1146	1334	1171	1810	1011	1339	1385	1428
Ni	471	1166	1419	840	1027	599	1266	487	986	1305	1212
V	243	65.2	78.8	118	155	173	114	170	107	99	106
Cu	38	58	60	105	119	119	80	128	77	33	50
Sc	28	14.4	8.5	17	16.8	20.5	15.1	19.3	11.2	9.96	10.2
Rb	52	187	98	99.3	86.2	100	22.9	68.3	106	92	99
Y	20	10.7	13.1	13.4	9.15	13.8	7.99	14	8.81	10	12
Nb	217	176	168	176	177	202	98.8	219	126	95.1	93.4
Ba	968	1254	1702	1971	1254	1523	627	1344	1164	1029	979
La	240	150	188	140	100	141	65	142	71.9	43	42
Ce	445	278	324	228	171	237	109	239	119	79	77
Pr	na	29.1	33	22.2	17.3	23.5	11.1	23.6	12.5	8.2	8.1
Nd	na	89.6	105	69.9	53.4	76.1	36.3	77.9	38.5	31	31
Sm	na	9.92	12.7	9	6.66	9.45	4.54	9.72	4.81	4.48	4.66
Eu	na	2.29	2.83	2.03	1.6	2.16	1.17	2.18	1.04	1.24	1.21
Gd	na	7.26	8.4	6.37	4.95	6.37	3.48	6.31	3.79	3.23	3.15
Tb	na	0.79	0.94	0.75	0.54	0.74	0.42	0.79	0.45	0.37	0.38
Dy	na	2.57	3.42	2.87	2.01	2.89	1.72	3.01	1.76	1.69	1.81
Ho	na	0.43	0.5	0.46	0.34	0.47	0.3	0.48	0.3	0.26	0.29
Er	na	0.86	0.97	1.15	0.72	1.15	0.72	1.3	0.77	0.63	0.68
Tm	na	0.09	0.11	0.13	0.09	0.17	0.09	0.16	0.09	0.074	0.081
Yb	na	0.47	0.69	0.8	0.58	0.92	0.58	0.9	0.67	0.43	0.48
Lu	na	<	<	0.10	0.1	0.13	0.1	0.13	0.11	0.06	0.064
Hf	na	9.15	4.66	2.53	2.07	2.3	1.47	2.46	1.9	1.72	1.73
Ta	na	9.52	10.1	10.2	12	11.4	6.07	11.1	8.57	6.64	6.5

Pb	na	11.4	14.3	10.9	8.62	7.82	2.41	7.46	8.24	3.37	3.77
Th	19	18	15.2	18.3	16.4	19.2	9.1	19.1	10.4	6.71	6.57
U	4	3.58	1.55	3.58	2.79	3.92	1.98	3.69	2.43	1.24	1.34
S	300	1000	2500	100	600	400	800	600	200	280	<20
Cl	na	na	na	170	500	190	150	220	280	na	na
Zn	na	na	na	87	78	84	63	89	67	52	49
Re (ppb) ¹	0.03	0.27	0.07	0.12	0.54	0.96	0.40	0.23	0.15	0.10	0.17
Os ¹	0.30	0.86	1.09	1.02	0.81	0.37	1.09	0.95	0.51	0.77	0.69
Ir ¹	0.33	0.48	0.59	0.83	0.54	0.38	0.37	0.15	0.20	0.70	1.00
Ru ¹	0.77	1.86	1.39	1.34	1.42	0.28	0.99	0.29	0.45	1.88	2.80
Rh ²	0.15	0.28	1.24	0.18	0.33	0.08	0.43	0.13	0.21	0.35	0.39
Pt ¹	0.41	1.38	1.28	1.43	1.43	1.33	1.72	1.15	1.05	1.96	1.99
Pd ¹	0.26	1.31	1.49	1.67	0.69	1.39	3.14	1.78	0.72	1.20	0.98
Au ²	0.70	1.04	1.84	0.26	0.48	0.68	0.75	0.66	0.94	0.43	0.47
Pd/Ir	0.80	2.74	2.55	2.01	1.28	3.66	8.42	11.87	3.67	1.72	0.98
Ir/Os	1.08	0.56	0.54	0.81	0.67	1.03	0.34	0.16	0.38	0.91	1.45
Ir/Ru	0.42	0.26	0.42	0.62	0.38	1.36	0.38	0.52	0.44	0.37	0.36
Ir/Rh	2.18	1.71	0.47	4.61	1.64	4.75	0.87	1.15	0.93	2.00	2.57
Pt/Ir	1.26	2.88	2.19	1.72	2.65	3.50	4.61	7.67	5.36	2.80	1.99

¹ HPA+ID+ICP-MS

² FA+ICP-MS

dl= value below detection limit; na=not analysed

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Table 2: Absolute amount of total procedural blanks (in picograms) for HPA-ID procedure (n=12)

	Ru	Pd	Re	Os	Ir	Pt
Average	0.24	0.66	0.11	0.49	0.11	3.16
Stdev	0.3	0.51	0.1	0.47	0.15	2.05
Lod (X + 3s)	1.14	2.2	0.42	1.91	0.55	9.32

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Table 3: Comparison of Results Obtained for Reference Materials by Isotope Dilution Analyses at UQAC with Certificate Values

	OKUM				LK-NIP				LLD
	UQAC		Geolabs		UQAC		UQAC		UQAC
	This run n=2	stdev	Certificate	stdev	This run n=1	Certificate +	working value	stdev n=3	
Ru ppb	4.72	0.15	4.25	0.3	0.58	0.44	0.48	0.015	0.021

Pd ppb	11.29	0.07	11.70	0.5	17.03	17.96	17.08	0.15	0.086
Re ppb	0.57	0.12	*0.566	0.04	0.79	n.d.	n.d.	n.d.	0.003
Os ppb	1.20	0.18	*0.79		0.51	n.d.	n.d.	n.d.	0.044
Ir ppb	1.11	0.23	0.99	0.07	0.16	0.19	0.15	0.02	0.004
Pt ppb	11.33	0.42	11.00	0.55	13.91	13.43	12.34	0.38	0.026

OKUM = Abtibi komatiite; LK-NIP = Niping Diabase both supplied by Geolabs, Ontario;

n.d. not determined; *for OKUM no certificate values are available for Os and Re so values from,

Savard et al. (2010) are presented. +For LK-NIP no standard deviations were given on the certificate

so in addition to certificate value working values and standard deviations obtained at UQAC by

Ni-FA-ICP-MS are presented for comparison; # Lower limit of detection for HPA-ID-ICP-MS analysis

Savard et al. (2010)

Table 1

Table 1: Whole rock data for Karelian and Kaapvaal kimberlites

Sample	KAI D21	16-002	16-002	9729	9729	9729	9729	9729	9729	P10
		26.95	23.83	5621	5611	5596	5603	5599	5604	
Craton	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Karelia	Kaapvaal
craton loc	margin	margin	margin	margin	margin	margin	margin	margin	margin	centre
pipe/dyke		d 16	d 16	p 10	p 14	p 2	p 5	p 3	p 9	Premier
Group	II	II	II	I	I	I	I	I	I	I
SiO ₂ (wt%)	23.44	42.95	36.07	35.28	34.96	32.08	35.99	29.69	39.43	39.81
TiO ₂	1.99	3.24	2.41	2.39	2.84	2.34	1.31	2.29	1.95	1.96
Al ₂ O ₃	3.14	4.01	2.30	5.02	3.48	5.43	2.74	4.88	3.62	2.11
Fe ₂ O ₃	7.97	9.93	9.79	9.59	11.49	11.79	9.47	11.29	9.32	9.36
MnO	0.28	0.14	0.15	0.19	0.19	0.26	0.17	0.35	0.15	0.14
MgO	15.02	21.68	29.47	24.19	29.96	22.58	28.39	20.89	26.95	27.31
CaO	22.48	5.44	4.87	8.30	3.78	10.09	7.27	12.59	6.19	7.16
Na ₂ O	dl	0.40	dl	0.21	0.14	0.10	0.14	0.11	1.05	0.06
K ₂ O	0.76	5.73	2.31	1.57	2.27	1.95	0.31	0.63	2.44	1.04
P ₂ O ₅	0.87	0.12	0.39	0.58	0.34	0.60	0.27	0.69	0.34	0.33
H ₂ O ⁺	na	na	na	10.14	9.68	8.96	10.50	10.50	9.36	na
LOI	na	na	na	na	na	na	na	na	na	8.96
C	na	na	na	0.74	0.47	1.01	1.27	1.90	0.10	na
Total	75.95	93.64	87.76	98.20	99.60	97.19	97.83	95.81	100.90	98.24
Zr (ppm)	217	319	149	103	63.7	94.4	52.8	96.6	69.1	80
Sr	1183	467	681	776	457	890	477	889	484	441
Co	na	80.8	85.7	62.8	78.2	59.9	80.5	52.7	67.8	88
Cr	750	1238	905	1146	1334	1171	1810	1011	1339	1385
Ni	471	1166	1419	840	1027	599	1266	487	986	1305
V	243	65.2	78.8	118	155	173	114	170	107	99
Cu	38	58	60	105	119	119	80	128	77	33
Sc	28	14.4	8.5	17	16.8	20.5	15.1	19.3	11.2	9.96
Rb	52	187	98	99.3	86.2	100	22.9	68.3	106	92
Y	20	10.7	13.1	13.4	9.15	13.8	7.99	14	8.81	10
Nb	217	176	168	176	177	202	98.8	219	126	95.1
Ba	968	1254	1702	1971	1254	1523	627	1344	1164	1029
La	240	150	188	140	100	141	65	142	71.9	43
Ce	445	278	324	228	171	237	109	239	119	79
Pr	na	29.1	33	22.2	17.3	23.5	11.1	23.6	12.5	8.2
Nd	na	89.6	105	69.9	53.4	76.1	36.3	77.9	38.5	31
Sm	na	9.92	12.7	9	6.66	9.45	4.54	9.72	4.81	4.48
Eu	na	2.29	2.83	2.03	1.6	2.16	1.17	2.18	1.04	1.24
Gd	na	7.26	8.4	6.37	4.95	6.37	3.48	6.31	3.79	3.23
Tb	na	0.79	0.94	0.75	0.54	0.74	0.42	0.79	0.45	0.37
Dy	na	2.57	3.42	2.87	2.01	2.89	1.72	3.01	1.76	1.69
Ho	na	0.43	0.5	0.46	0.34	0.47	0.3	0.48	0.3	0.26
Er	na	0.86	0.97	1.15	0.72	1.15	0.72	1.3	0.77	0.63
Tm	na	0.09	0.11	0.13	0.09	0.17	0.09	0.16	0.09	0.074
Yb	na	0.47	0.69	0.8	0.58	0.92	0.58	0.9	0.67	0.43

Table 2: Absolute amount of total procedural blanks (in picograms) for HPA-ID procedure (n=12)

	Ru	Pd	Re	Os	Ir	Pt
Average	0.24	0.66	0.11	0.49	0.11	3.16
Stdev	0.3	0.51	0.1	0.47	0.15	2.05
Lod (X + 3s)	1.14	2.2	0.42	1.91	0.55	9.32

Table 3: Comparison of Results Obtained for Reference Materials by Isotope Dilution Analyses at UQAC Certificate Values

	OKUM				LK-NIP			
	UQAC		Geolabs		UQAC	Geolabs	UQAC	UQAC
	This run n=2	stdev	Certificate	stdev	This run n=1	Certificate +	UQAC working value	UQAC stdev n=3
Ru ppb	4.72	0.15	4.25	0.3	0.58	0.44	0.48	0.015
Pd ppb	11.29	0.07	11.70	0.5	17.03	17.96	17.08	0.15
Re ppb	0.57	0.12	*0.566	0.04	0.79	n.d.	n.d.	n.d.
Os ppb	1.20	0.18	*0.79		0.51	n.d.	n.d.	n.d.
Ir ppb	1.11	0.23	0.99	0.07	0.16	0.19	0.15	0.02
Pt ppb	11.33	0.42	11.00	0.55	13.91	13.43	12.34	0.38

OKUM = Abtibi komatiite; LK-NIP = Niping Diabase both supplied by Geolabs, Ontario;

n.d. not determined; *for OKUM no certificate values are available for Os and Re so values from, Savard et al. (2010) are presented. +For LK-NIP no standard deviations were given on the certificate so in addition to certificate value working values and standard deviations obtained at UQAC by Ni-FA-ICP-MS are presented for comparison; # Lower limit of detection for HPA-ID-ICP-MS analysis Savard et al. (2010)

Figure 1

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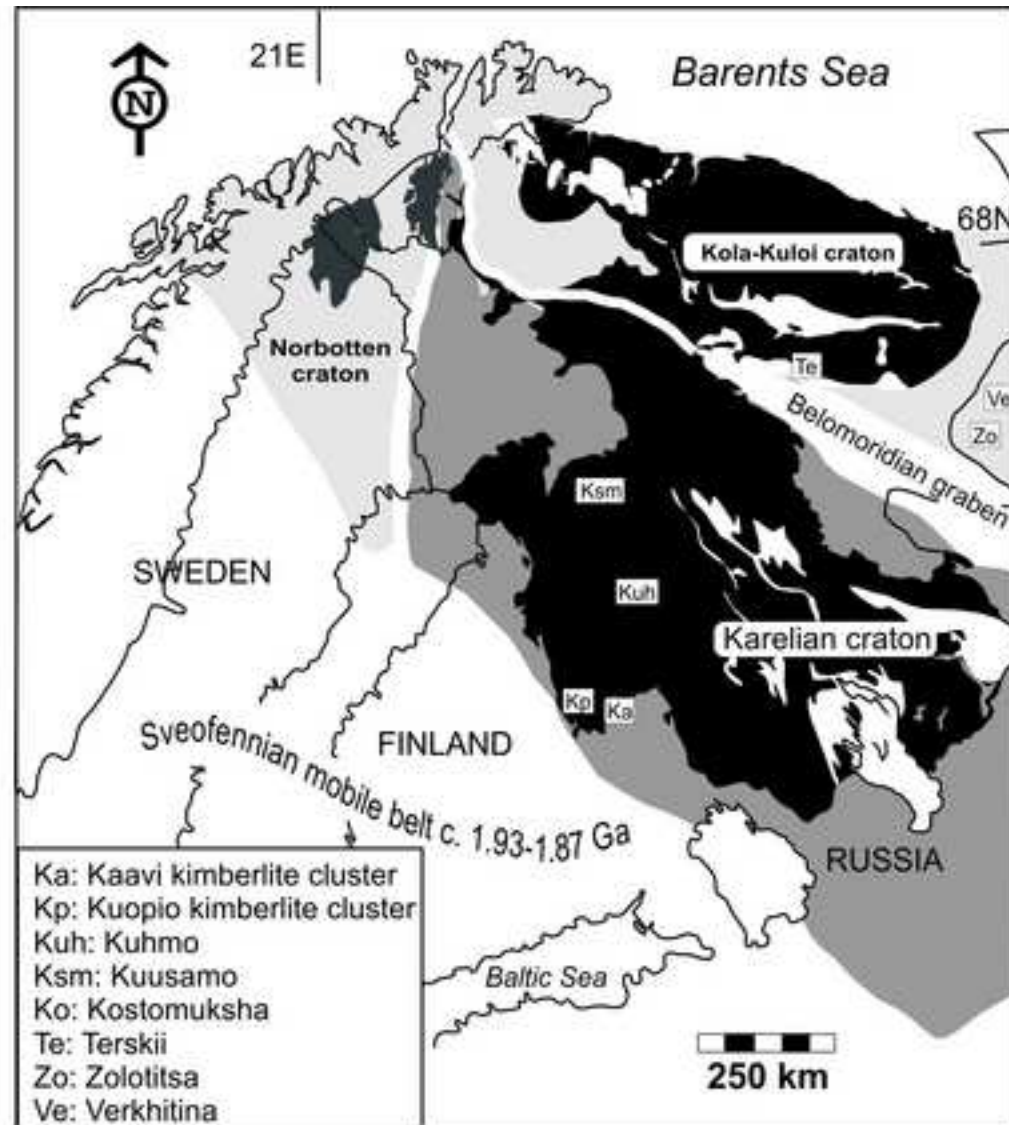


Figure 2
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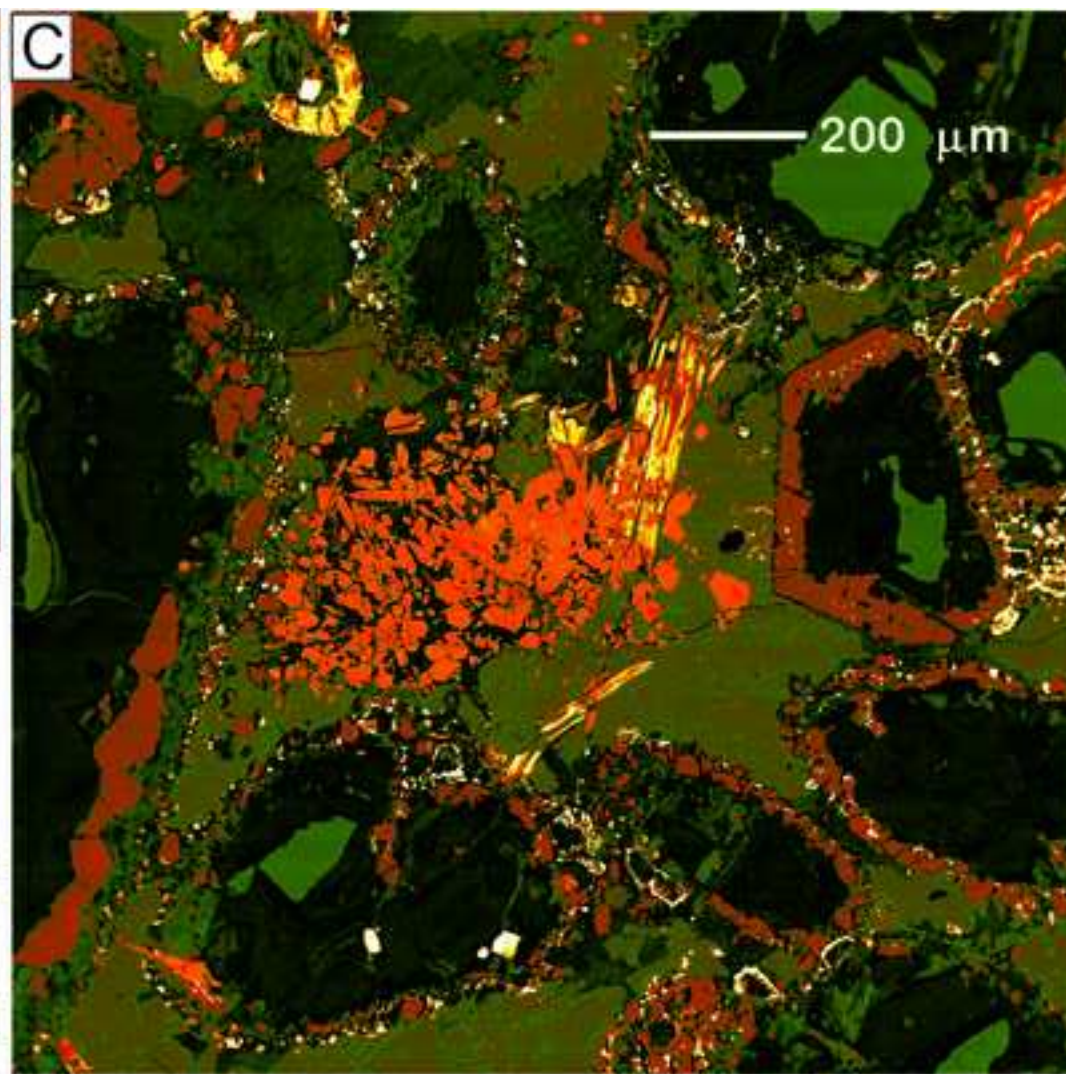
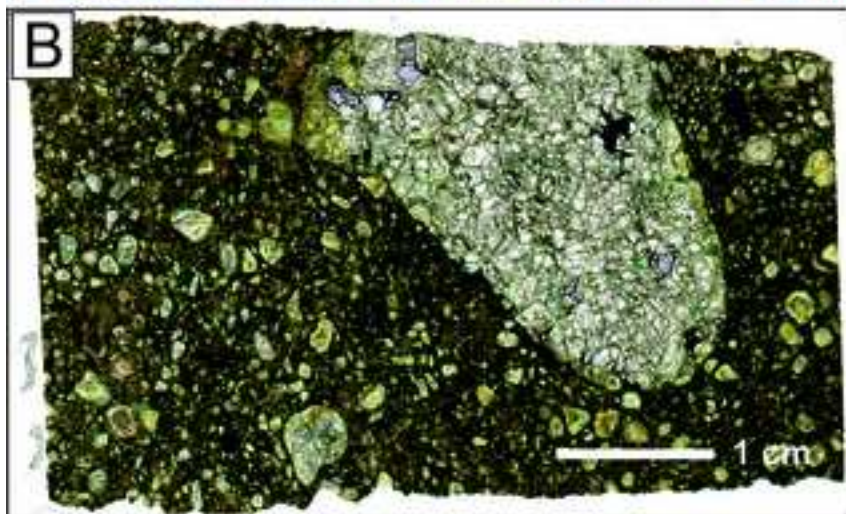
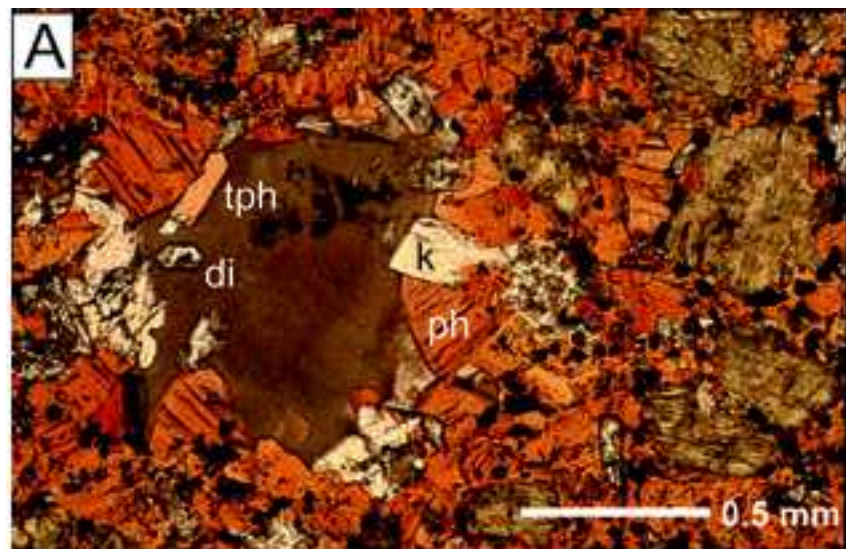


Figure 3
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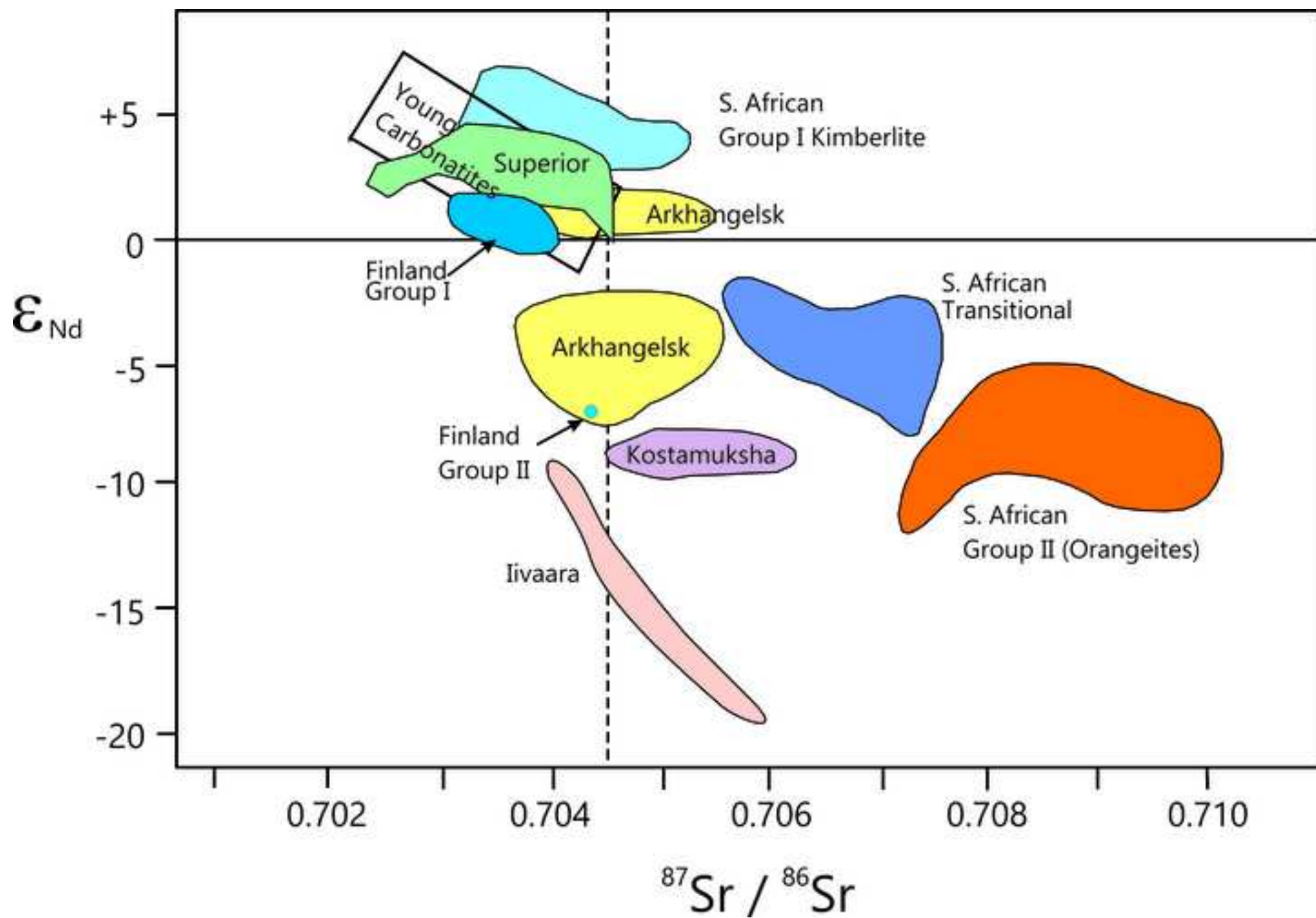


Figure 4

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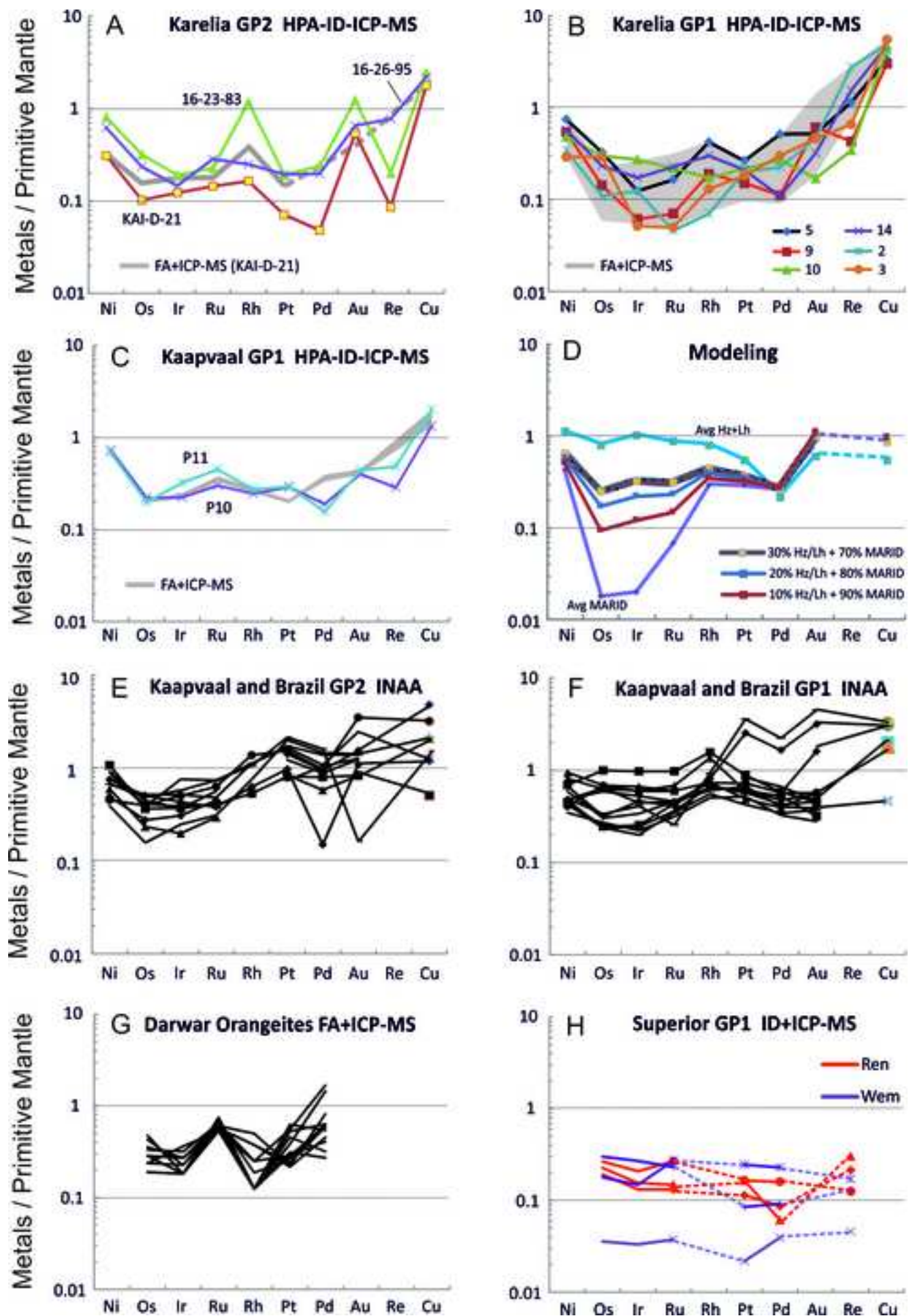


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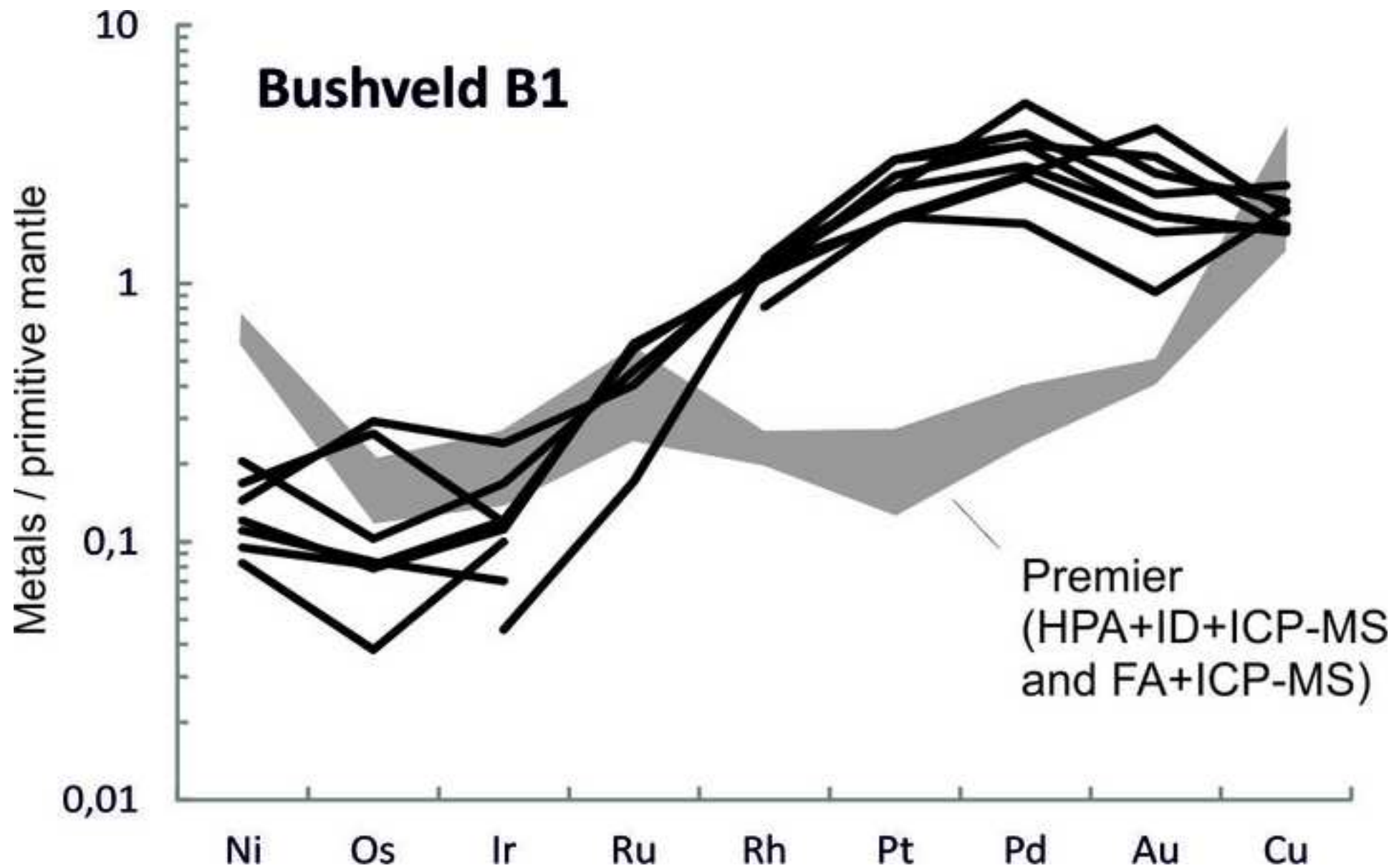
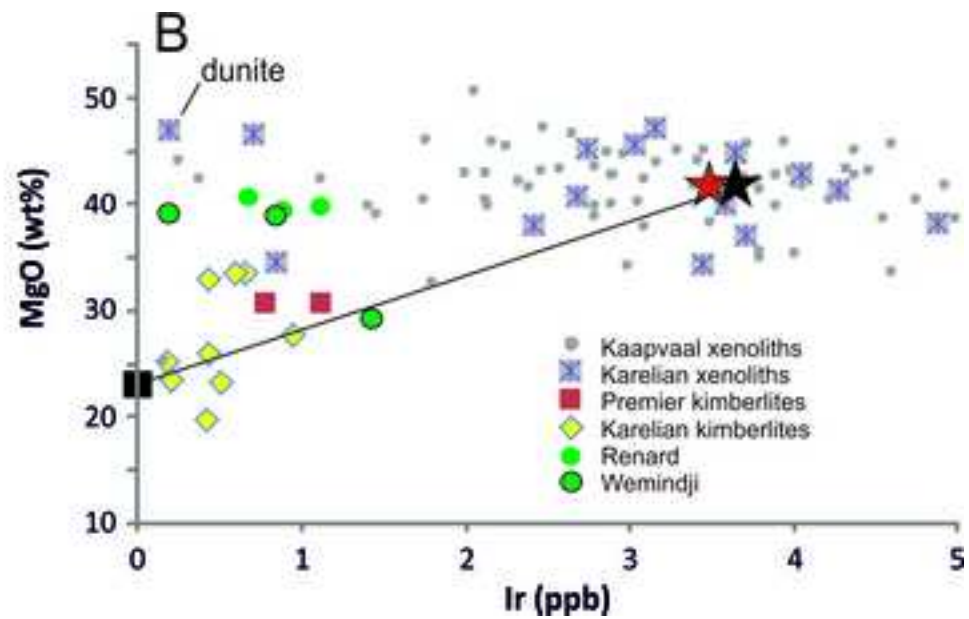
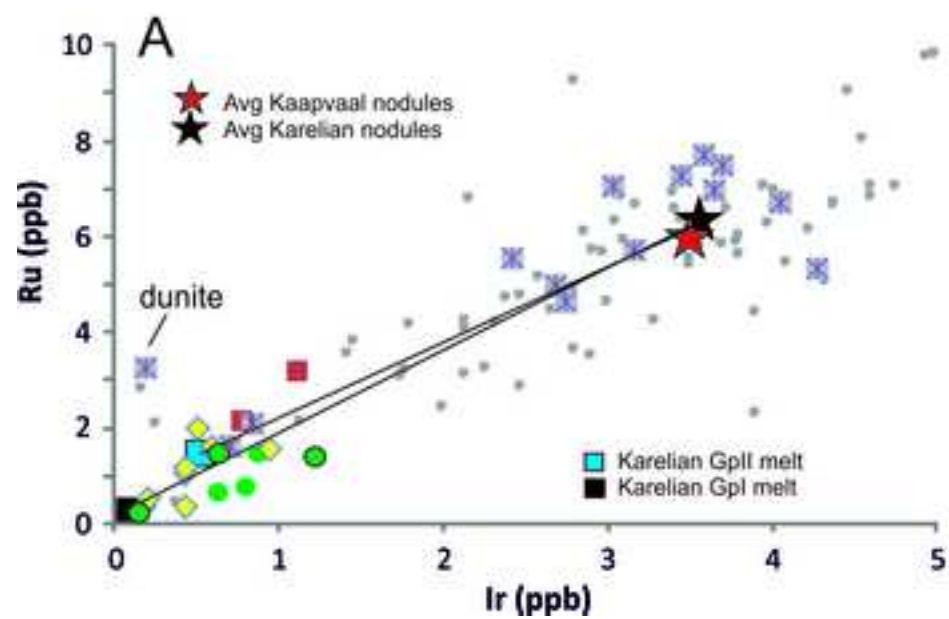


Figure 6
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Electronic Annex 1

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Electronic Annex 2

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