

1 **An assessment of the mantle and slab components in the magmas of**
2 **an oceanic arc volcano: Raoul Volcano, Kermadec arc**

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14 **Abstract**

15 Raoul Volcano occupies a simple oceanic subduction setting in the northern part of
16 the Kermadec Arc on the Pacific-Australian convergent plate boundary. The primary
17 inputs to the magmatic system that feeds the volcano are a subduction component
18 derived from the subducting old Pacific oceanic lithosphere and its veneer of pelagic
19 sediment, and the overlying peridotitic mantle wedge. Conservative trace elements
20 that are very incompatible during mantle melting are relatively depleted in Raoul
21 lavas indicating a source that has been depleted during an earlier melting event. Major
22 element co-variations indicate magma genesis by 25% near fractional melting of a
23 mantle source that is weakly depleted (2% melt extraction) relative to a fertile MORB
24 source. An important influence on the composition of the mantle component is
25 progressive melt extraction coupled with minimal advection of fresh material into the
26 sub-arc zone followed by melt extraction from a melting column beneath the
27 spreading centre of an adjacent back arc basin. High field strength element and rare
28 earth element systematics indicate involvement of a subduction-related component of
29 constant composition. Two fluid components can be distinguished, one enriched in
30 large ion lithophile elements inferred to be an aqueous fluid that is continuously added
31 to the ascending melt column and the other a less mobile fluid that transfers Th. A
32 homogeneous subduction-related component of constant composition and magnitude

33 arises if the slab-derived flux migrates from the slab-mantle interface to the sub-arc
34 melting column by repeated episodes of amphibole formation and decomposition its
35 composition is then governed by the distribution coefficients of pyroxene and its
36 magnitude by the degree of amphibole saturation of mantle peridotite. The results
37 from Raoul Volcano are comparable to those from other oceanic subduction-related
38 arcs such as South Sandwich and Marianas suggesting that this is a general model for
39 oceanic arcs.

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41 *Keywords:* Kermadec arc, oceanic arcs, subduction zones, magma genesis.

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58 **1. Introduction**

59 Subduction related magmas are complex materials made up of components derived
60 from multiple sources and assembled by a variety of processes. In currently popular
61 models the components and processes involved in the formation of a typical arc-type
62 magma include a contribution from the subducting slab, transfer of this component to
63 the overlying mantle wedge, melting in the wedge to produce a primitive magma and
64 profound modification of these primitive melts by crystallization, fractionation, melt
65 mixing and assembly of the final product (e.g. Price et al., 2005; Eichelberger et al.,
66 2006). Subduction-related magmas are characterized by their enrichment in large-ion
67 lithophile elements (LILE) and depletion of high-field strength elements (HFSE)
68 relative to mid-ocean ridge basalts (MORB) (e.g. Gill 1981; Pearce, 1983).

69 Conventional models of subduction related magma genesis link these attributes to the
70 transfer of a hydrous LILE - bearing HFSE depleted component from the subducting
71 slab to the overlying mantle (e.g. Tatsumi et al., 1986; McCulloch and Gamble, 1991;
72 Pearce and Peate, 1995).

73 In terms of chemical mass balance in subduction related magmatic systems,
74 elements are termed conservative if they are not represented in the slab component
75 and slightly (<40%), moderately (40-80%) or highly (>80%) non-conservative as their
76 contribution from the slab increases relative to the mantle component (Pearce and
77 Peate, 1995). The distinction between conservative and non-conservative elements is
78 thus determined by transfer across the interface between the subducting slab and the
79 mantle wedge. Potentially, the slab-derived component may be modified en route
80 from the slab to the sub-arc melt generation zone by scavenging of some elements,
81 loss of other elements, or by isotopic exchange (Navon and Stolper, 1987;
82 Hawkesworth et al., 1991; Stolper and Newman, 1994; Pearce and Peate, 1995).

83 Both the subducted oceanic lithosphere and its overlying sediment veneer are
84 potential sources of the slab derived component. Aqueous fluids generated in the slab
85 have high LILE/HFSE ratios (e.g. Brenan et al., 1995; Keppler, 1996) and migrate
86 across the mantle wedge in time scales of the order of 30-50 ka (Turner et al., 1996;
87 1997; Elliot et al., 1997). There is also evidence for a component which migrates on
88 much shorter timescales (Davies, 1999; Handley et al., 2008; Caulfield et al., 2008).
89 Conversely silicic melts derived from subducting sediment may bear both LILE and
90 HFSE (McDermott et al., 1993; Nichols et al., 1994). Such melts probably leave the
91 slab at shallower depths and may reside in the mantle wedge for several Ma before
92 reaching the sub-arc melt generation zone (Turner and Hawkesworth, 1997).

93 Raoul Volcano (29°14'50" S 177°55'07" W) is located in a particularly simple part
94 of the Tonga Kermadec arc (Fig.1) in what is arguably one of the simplest subduction
95 settings on Earth. Raoul is the only volcano in the Kermadec Arc that has significant
96 subaerial exposure and the lava sequences exposed on the island represent the longest
97 documented time span ($\sim 10^4$ - 10^5 years) and the greatest known variety of rock types
98 of any Kermadec volcano. Raoul Island is small (maximum dimensions of 10 by 7
99 km, total area 29.4 km²) but is the summit portion of a much larger volcanic massif
100 that rises 900 m from the crest of the Kermadec Ridge and has a volume of 214 km³.
101 Raoul Volcano is located in the Northern Kermadec arc segment (Smith and Price,
102 2006) where the volcanoes rise from a relatively shallow Kermadec Ridge. In this
103 segment there is minimal sediment subducting beneath the arc and there is no
104 continental component to this. Therefore erupted magmas should contain a chemical
105 signature free from continental input.

106 In this paper we use geochemical data from a suite of basaltic and andesitic lavas
107 from Raoul Island to assess the relative roles of the different components and

108 processes that have contributed to the magmatic system that built the volcano. The
109 data set on which the paper is based comprises a subset of samples that are
110 representative of a larger database of 200 lava samples for which major and trace
111 element analyses analysed by X-Ray Fluorescence are available. These representative
112 samples have been analysed for minor trace elements and isotope ratios by ICP-MS
113 and thermal ionization mass spectrometry (Table 1).

114 Most Raoul lavas are moderately to strongly porphyritic, some contain up to 48%
115 phenocrysts (typically 20-30%) and a minority are sparsely phyrlic to aphyric with <
116 5% phenocrysts. All have a simple anhydrous mineral assemblage dominated by
117 plagioclase accompanied by lesser amounts of clinopyroxene and minor olivine,
118 orthopyroxene and spinel. Hornblende is not found in any Raoul lava although it does
119 occur in xenoliths. The sparsely phyritic and aphyric samples comprise a relatively
120 small group ranging from basalt to andesite. Silicic lavas are a subordinate but
121 nonetheless significant component of the Raoul suite but as they have been effectively
122 modelled as the products of crustal melting (Smith et.al., 2006) they are not relevant
123 to this assessment of the sub-crustal processes and components beneath an oceanic
124 arc.

125 Porphyritic samples show a variety of disequilibrium petrographic features that
126 indicate that they are mixtures of silicate liquid and entrained crystals rather than
127 crystallisation products of melts, and this includes basaltic and basaltic andesite
128 compositions that have relatively high Mg# (Fig 2). The aphyric samples are
129 interpreted to represent magmatic liquids but their compositions are clearly
130 geochemically evolved. In this study we have placed emphasis on their chemical
131 compositions as a means of assessing the inputs of the system as a whole while

132 acknowledging that they are the fractionated products of a primitive arc magma that is
133 not represented in the exposed rocks of the volcano.

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135 **2. Assessing the mantle contribution**

136 In the sense that the origin of arc-type magmas is in the mantle wedge above the
137 subducting slab, the behavior of conservative elements in a subduction environment is
138 directly comparable with that beneath oceanic spreading centers. Flat MORB
139 normalized HFSE abundance patterns and low MORB normalized HFSE values (<1)
140 typical of most low-SiO₂ subduction-related lavas indicate that these elements are
141 conservative and that the degree of mantle melting beneath volcanic arcs exceeds that
142 beneath spreading centres (eg Ewart and Hawkesworth, 1987; Pearce and Parkinson,
143 1993). However, some subduction-related lavas have negative anomalies for
144 particular HFSE and others have positive anomalies. Variations also occur in the
145 ratios of conservative elements such as Ta/Yb, Nb/Zr, Zr/Ti, Y/Sc and Ti/V. Both the
146 frequency and magnitude of these deviations from MORB-like values mimic a
147 sequence of decreasing distribution coefficient during melting of a spinel lherzolite
148 source. This dependence on conservative element distribution coefficient (D_C)
149 suggests that co-variations are sensitive indicators of mantle depletion or enrichment
150 events (Ewart and Hawkesworth, 1987; McCulloch and Gamble, 1991; Pearce and
151 Parkinson, 1993; Woodhead et al., 1993). These observations are consistent with
152 recent work in the Tongan Arc where strongly sub-chondritic Nb/Ta ratios point to the
153 involvement of a highly depleted source (Caulfield et al., 2008).

154 Fig. 3 illustrates the co-variations in Raoul lavas with respect to a fertile MORB
155 mantle (FMM) source composition. The FMM-normalised pattern of Raoul lavas is
156 comparable to that of average MORB for most moderately incompatible conservative

157 elements. Significantly, elements that are more incompatible than Y have lower
158 FMM-normalised abundances than those of MORB and this trend increases in
159 magnitude as D_C decreases. This is in spite of the fact that Raoul lavas are chemically
160 evolved. The relative depletion in elements such as Co, Mg, Cr and Ni can be
161 explained by their evolved chemistry.

162 Element ratios in which a conservative element is the numerator and another with
163 higher D_C is the denominator are consistently less for average MORB and vice-versa.
164 For example Ti/V in an average aphyric Raoul lava with <55wt% SiO₂ is 13
165 compared with 25 for MORB whereas Ti/Zr in aphyric Raoul lava is 129 compared
166 with 103 for MORB. Similar FMM-normalised trends and conservative element ratios
167 have been attributed to re-melting of a MORB-source mantle from which a small melt
168 fraction has been removed, the earlier event being responsible for depletion in highly
169 incompatible elements (Gamble et al., 1993; Pearce and Parkinson, 1993; Woodhead
170 et al., 1993).

171 A difference from the MORB pattern is a positive V_{FMM} anomaly in aphyric
172 Raoul lavas. This may reflect melting under more oxidizing conditions because the
173 oxidation state of V is sensitive to fO_2 and there is a marked difference between $D_{V(5+)}$
174 (~ 0.05) and $D_{V(3+)}$ (~ 5) for mantle melting, with the speciation of V changing rapidly
175 near the QFM buffer (Shevais, 1982; Carmichael and Ghiorso, 1990).

176 The sub-arc mantle beneath Raoul Volcano has the geochemical and geothermal
177 characteristics of a Pacific MORB source (Ewart and Hawkesworth, 1987; Hergt and
178 Hawkesworth, 1994; Pearce et al., 2007). The sub-arc mantle may also be mildly
179 depleted in incompatible elements relative to a fertile MORB mantle source. This
180 situation can be explained if mantle that had melted to generate new crust in the
181 northern Havre Trough was subsequently advected into the sub-arc region (e.g. Ewart

182 and Hawkesworth, 1987, Caulfield et al., 2008). Replenishment of the sub-arc mantle
183 source can also occur by advection because of mechanical coupling at the slab-wedge
184 interface where mantle adjacent to the descending slab is dragged down and a
185 compensatory trench-ward flow is established in the overlying asthenosphere (e.g.
186 Davies and Stevenson, 1992; Caulfield et al, 2008).

187 Most Raoul lavas have $\text{MgO} < 6 \text{ wt.}\%$, $\text{Mg\#} < 55$, and none have the geochemical
188 characteristics expected of primitive magma. Instead, they have undergone
189 modification by fractional crystallization and crystal accumulation. One technique for
190 removing the effects of fractional crystallization involves fitting regression lines for
191 each element to MgO , and then extrapolating the element abundance to an MgO
192 content of interest, typically 8 or 9 wt.% (here, Ca_8 will be used to refer to the CaO
193 content extrapolated to $\text{MgO} = 8.0 \text{ wt.}\%$, etc). Although lavas with 8-9 wt. % MgO do
194 not represent primary magmas, this extrapolation does provide a common reference
195 point for the comparison of different magmatic suites and has been used with some
196 success in studies of MORB and continental flood basalt petrogenesis (e.g., Klein and
197 Langmuir, 1989; Turner and Hawkesworth, 1995). This style of regression also
198 removes some of the effects of crustal contamination if that is coupled with
199 fractionation. The technique assumes that the fractionating assemblage is of constant
200 composition throughout the range of the extrapolation, and that the analyses on which
201 the regression equations are based represent magmas. The major element composition
202 of Raoul lavas were recalculated for $\text{MgO} = 8 \text{ wt.}\%$ by linear regression (Table 2).
203 The linear regression equations were calculated using only the group of aphyric lavas
204 to derive equations that were then applied to all lavas with $< 57 \text{ wt.}\% \text{ SiO}_2$.

205 In the absence of a terrigenous sedimentary component CaO and Al_2O_3 are
206 conservative during subduction-related magma genesis, although this may reflect

207 masking of any subduction-related component by the relatively high concentration of
208 these elements in the mantle (e.g., Pearce and Parkinson, 1993). Strongly depleted
209 mantle has lower $\text{CaO}/\text{Al}_2\text{O}_3$ values than normal mantle because $D_{\text{Ca}} < D_{\text{Al}}$ during
210 melting. Therefore, magma generated by melting of depleted mantle is expected to
211 have $\text{CaO}/\text{Al}_2\text{O}_3 < 0.75$, which is the MORB value at $\text{MgO} = 7.5$ wt.% (Pearce and
212 Parkinson, 1993). For the regressed Raoul lavas, Ca_8/Al_8 varies from 0.69-0.88 and
213 averages 0.80. The high Ca_8/Al_8 values of Raoul lavas are not artefacts of plagioclase
214 accumulation because if the dataset is restricted only to aphyric lavas the ratio actually
215 increases to an average of 0.85. Both elements were therefore unaffected (or equally
216 affected) by the depletion event indicated by low Nb_{FMM} , Zr_{FMM} , and Ti_{FMM} (Fig. 4).

217 Melting of depleted mantle is also expected to generate melts with higher
218 Al_8/Ti_8 and Ca_8/Ti_8 than fertile mantle, as $D_{\text{Ti}} < D_{\text{Al}}$ and $D_{\text{Ti}} < D_{\text{Ca}}$. The regressed
219 Raoul analyses form a linear trend with positive slope on a plot of Al_8/Ti_8 versus
220 Ca_8/Ti_8 (Fig. 4). Aphyric lavas have Al_8 and Ca_8 equivalent to that of MORB at MgO
221 $= 7.5$ wt.% (calculated from Pearce and Parkinson, 1993), whereas porphyritic lavas
222 extend towards and into the field representing experimental melts from a depleted
223 mantle source. The effect of crystal accumulation on the regressed analyses was
224 modeled by adding plagioclase (An_{87}), clinopyroxene ($\text{En}_{46}\text{Fs}_{15}\text{Wo}_{39}$) and olivine
225 (Fo_{70}) to an aphyric lava, and then calculating Al_8/Ti_8 and Ca_8/Ti_8 . Vectors
226 representing the addition of these phases are depicted on Fig. 4, and demonstrate that
227 the trend of increasing Al_8/Ti_8 and Ca_8/Ti_8 from aphyric lavas through the range of
228 porphyritic lavas is primarily an artefact of plagioclase accumulation. Other
229 Kermadec lavas have significantly higher Al_8/Ti_8 and Ca_8/Ti_8 than Raoul aphyric
230 lavas (Fig. 3). The Kermadec array overlaps that for strongly plagioclase-phyric Raoul
231 lavas on Figure 4.

232 In summary, evidence for a depleted (relative to MORB) mantle source
233 beneath Raoul comes from low values of Nb_{FMM} , Zr_{FMM} , and Ti_{FMM} . The degree of
234 depletion is too small to affect elements of greater D_C during melt extraction, such as
235 Ca and Al and their concentrations in the sub-arc mantle are comparable to those in
236 normal MORB source mantle.

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238 *2.1 Melting in the mantle wedge*

239 In widely accepted models, subduction-related magmas are linked to fluxing
240 by a hydrous component transferred from the subducting slab (e.g., Tatsumi et al.,
241 1986; Davies and Bickle, 1991; McCulloch and Gamble, 1991; Davies and Stevenson,
242 1992; Pearce and Peate, 1995). The fluid (or melt) derived from the slab reacts with
243 peridotite in the overlying mantle wedge to form amphibole, and this component is
244 progressively transferred to hotter regions of the mantle wedge by a complex cycle
245 involving amphibole decomposition at higher pressure and amphibole formation at
246 shallower depth. This cyclical process is limited by the amphibole-saturated peridotite
247 solidus (3.0 GPa, 1150 °C); above this, peridotite is too hot for new amphibole to
248 form and the mantle-melt mix ascends as a melting column. As the column rises
249 further melting is due to decompression, analogous to processes believed to occur
250 beneath spreading centers (Pearce and Parkinson, 1993). Note however, that although
251 this model is generally consistent with theoretical constraints the actual transfer
252 process of a hydrous fluid from the subducting slab is likely to be complex and multi-
253 staged (c.f. Davies 1999).

254 Theoretical and experimental studies of decompression melting beneath
255 spreading centers have led to the development of near-fractional melting models

256 (O'Hara, 1985 McKenzie and Bickle, 1988; Klein and Langmuir, 1987; 1989; Kinzler
257 and Grove, 1992). In this process, small melt fractions (~1 %) segregate from the
258 rising melting column, do not equilibrate with overlying mantle, and are aggregated at
259 shallower depth. Earlier melts from deeper in the melting column are enriched in
260 incompatible elements, whereas later melts from the higher, more depleted, column
261 are less enriched in these elements. Inefficient melt pooling produces aggregate
262 magmas with a range of compositions, each reflecting the average composition of its
263 amalgamated melts.

264 The co-variation of Na_8 and Fe_8 in MORB provides further insight into mantle
265 melting processes (Klein and Langmuir, 1987; 1989). Sodium is highly incompatible
266 during melting of spinel lherzolite as $D_{\text{Na}} \sim D_{\text{Zr}}$ (Sun and McDonough, 1989) and its
267 concentration in the melt decreases as the extent of melting increases. The Fe content
268 of a mantle melt increases with pressure and so the global $\text{Na}_8 - \text{Fe}_8$ array for MORB
269 has a negative slope (Fig. 5). High Na_8 - low Fe_8 lavas erupt at deep spreading centers
270 where the mantle temperature is inferred to be cool and the melting column short.
271 Conversely, low Na_8 - high Fe_8 lavas erupt at shallow spreading centers where the
272 mantle is inferred to be hottest and the melting column longest. Their geochemistry
273 indicates a large degree of melting at a greater average depth.

274 Raoul aphyric lavas plot on an extrapolation of the global MORB $\text{Na}_8 - \text{Fe}_8$
275 array to lower Na_8 and higher Fe_8 (Fig. 5). The low Na_8 - high Fe_8 end of the MORB
276 array can be generated by approximately 18 % total melting at an average pressure of
277 1.5 GPa (Kinzler and Grove, 1992). By analogy, the data for Raoul suggest a longer
278 mantle melting column that begins to melt at greater depth and undergoes more
279 melting. Although the earlier mantle depletion event indicated by low values of
280 Nb_{FMM} , Zr_{FMM} , and Ti_{FMM} in Raoul lavas will have reduced the Na content of the

281 mantle source, Fe_8 should not be affected by that event. If the Na content of aphyric
282 lavas includes a significant subduction-related component, then the Na content of the
283 mantle-derived component must be even lower than that indicated on Fig. 5. A
284 conclusion from these data is that the low Na_8 and high Fe_8 values of Raoul lava are
285 best explained by a greater degree of mantle melting than is generally the case
286 beneath any spreading centre. Most porphyritic suite lavas from Raoul form a diffuse
287 array with slightly positive slope, extending from the aphyric lavas toward lower Na_8
288 and Fe_8 values. The effect of crystal accumulation on Na_8 and Fe_8 , shown as vectors
289 on Fig.5 is modeled by adding plagioclase (An_{87}) clinopyroxene ($En_{46}Fs_{15}Wo_{39}$) and
290 olivine (Fo_{70}) to an aphyric lava.

291 Lavas from other Tonga-Kermadec volcanoes have lower Fe_8 coupled with
292 either comparable Na_8 (Tonga) or higher Na_8 (Kermadec). The higher Na_8 and lower
293 Fe_8 may indicate less melting at a shallower average depth than that beneath Raoul.
294 Conversely, the similar Na_8 but lower Fe_8 would suggest comparable degrees of
295 melting at shallower depth. Further evidence of a high degree of melting beneath
296 Raoul can be found in the abundances of conservative elements. Both Nb and Yb are
297 highly incompatible during melting of spinel lherzolite, with $D_{Nb} < D_{Yb}$ (Sun and
298 McDonough, 1989). In consequence, Nb/Yb is a sensitive measure of mantle melting
299 and depletion because melt extraction will deplete Nb relative to Yb (Pearce and
300 Parkinson, 1993). Nb abundance is plotted against Yb content in Fig. 6. Values of Nb
301 and Yb in representative aphyric and porphyritic suite lavas have been regressed to
302 $MgO = 9$ wt.% using the procedure outlined earlier and the higher value of MgO. 9
303 wt.% versus 8 wt.% was chosen for consistency with the calibration of the Nb₉ - Yb₉
304 array (Pearce and Parkinson, 1993).

305 Most of the Raoul lavas form a cluster in Nb₉ -Yb₉ space (Fig. 6). If the
306 diagram is correctly calibrated, then they were generated by 15-35 % melting of a
307 mantle source ranging in composition from FMM to a source depleted by 4 % melt
308 extraction relative to FMM. An average Raoul lava would be generated by 25 %
309 melting of a source depleted by 2 % melt extraction relative to FMM. This is broadly
310 consistent with the evidence of >18 % melting from Na (Fig. 6). The Nb₉ / Yb₉ ratio is
311 not sensitive to the effects of phenocryst contamination, and aphyric and porphyritic
312 suite lavas overlap. However, if Nb (or possibly Yb) are contributed from a
313 sedimentary component it follows that the wedge had a lower Nb and Yb content at
314 9% MgO which would infer greater degrees of depletion and larger amounts of
315 melting.

316 Analyses from other intra-oceanic arcs yield comparable results (Pearce and
317 Parkinson, 1993; Pearce et al., 1995; Peate et al., 1997). South Sandwich lavas require
318 a slightly more depleted source and higher degree of melting, Mariana lavas require
319 slightly less melting of a less depleted source, and New Hebrides lavas require
320 slightly more melting of an FMM source (Fig.6). In contrast, lavas from continental
321 margin arcs and those lacking active backarc extension (e.g., the Aleutians) have
322 lower degrees of melting of mantle enriched relative to FMM.

323 **3. Assessing the Subduction-Related Component**

324 Although, the composition of the subduction-related component in Raoul lavas
325 can be appraised in a general way from a MORB-normalised plot (Fig 7) detailed
326 evaluation rests on the assumption that mantle melting beneath the volcano is
327 analogous to that taking place beneath spreading centers. Theoretical studies and
328 conservative element systematics in subduction-related lavas suggest that this
329 assumption is valid, at least for a small volume hydrous flux (Pearce and Parkinson,

330 1993). Quantifying the magnitude of the subduction-related component for each
331 element is then dependent on seeing through the combined effects of near-fractional
332 melting, inefficient melt pooling to form aggregate magmas, polybaric open-system
333 fractional crystallisation, and late-stage crystal accumulation.

334 We have approached the problem by using the co-variation of incompatible
335 element abundances and Nb/Yb ratios (Pearce, 1983; Pearce et al., 1995; Pearce and
336 Peate, 1995). The conceptual basis for this approach is that Nb/Yb is highly sensitive
337 to near-fractional melting, melt pooling, and previous mantle depletion or enrichment
338 events, chiefly because $D_{\text{Nb}} < D_{\text{Yb}}$ during melting of spinel lherzolite (Sun and
339 McDonough, 1989) and so plotting other elements or element ratios against Nb/Yb
340 effectively normalizes them for variations in these parameters. Two assumptions are
341 inherent in this approach. Firstly that both Nb and Yb are conservative elements, and
342 neither is present in the subduction-related component for Raoul lavas, values of
343 Nb_{FMM} less than MORB and Yb_{FMM} equivalent to MORB provide strong evidence that
344 this is so (Fig. 3). Secondly, that both Nb and Yb are equally affected by fractional
345 crystallization or crystal accumulation. This is a good approximation, because $D_{\text{Nb}} \sim$
346 D_{Yb} for plagioclase, olivine, and pyroxene, and both are very small.

347 MORB-normalised plots of the form X/Yb versus Nb/Yb, (where X is an
348 incompatible element) produce an array of positive slope (i.e., increasing X/Yb with
349 increasing Nb/Yb) centered on the average MORB composition (Pearce and Peate,
350 1995). The array is interpreted as an artefact of the melting process. Early melts from
351 deep in the melting column have high X/Yb and Nb/Yb, whereas later melts from
352 higher in the now depleted column have lower X/Yb and Nb/Yb. This reflects the
353 situation where $D_{\text{X}} < D_{\text{Yb}}$ and $D_{\text{Nb}} < D_{\text{Yb}}$ during mantle melting. A negative array
354 slope would develop for $D_{\text{X}} > D_{\text{Yb}}$. The range of X/Yb and Nb/Yb in melts is partly

355 preserved in MORB because pooling to form aggregate magmas is inefficient, and not
356 all melts are represented by any one aggregate magma.

357 For subduction-related lavas, the equivalent plots should return the mantle
358 array if X is a conservative incompatible element. If X is a non-conservative
359 incompatible element, the slope and location of the array depends upon the
360 composition of the mantle, the subduction-related component, and how they are
361 mixed prior to melting.

362 Four distinct trends explain the behavior of non-conservative incompatible
363 elements in subduction zones and these are illustrated in Fig.8. Variable X/Yb at
364 constant Nb/Yb (trend A) results from the addition of a variable subduction-related
365 component to a mantle of constant composition. Near-fractional melting introduces
366 scatter parallel to the MORB array for both X/Yb and Nb/Yb, generating a rectangular
367 array centred along line A. Nearly constant X/Yb but variable Nb/Yb (trend B) arises
368 from the addition of a constant subduction-related component to a variable mantle
369 composition. Near-fractional melting enhances the spread in Nb/Yb and displaces
370 X/Yb values in directions parallel to the MORB array, leading to a rectangular array
371 centered on line B. A trend parallel to the MORB array but offset to higher X/Yb and
372 lower Nb/Yb (trend C) is best explained by a combination of events involving melt
373 extraction which generates a depleted mantle of constant composition (Cm) together
374 with a subduction-related component of constant composition added to the depleted
375 mantle to produce composition C at the end of the vertical open-headed arrow. Near-
376 fractional melting of the mix then generates the trend parallel to the MORB array.
377 Trends lying at an angle to the MORB array, along which SiO₂ increases from one
378 end (D1) to the other (D2) are best explained as a Type C array (here offset to an
379 enriched mantle source) accompanied by progressive late-stage assimilation of crustal

380 material. Contour lines (dashed) representing the proportion of element X derived
381 from the subduction-related component are parallel to the MORB array on these plots

382 We have assessed the proportion of each incompatible element contributed by
383 the subduction related component in Raoul lavas using a series of X/Yb versus Nb/Yb
384 plots (Fig.9). Plots of Zr/Yb and Ba/Yb versus Nb/Yb highlight the contrasting
385 behavior of conservative and highly non conservative elements during subduction-
386 related magma genesis. All Raoul lavas have Nb/Yb < average MORB, reflecting
387 their derivation from a depleted mantle source as discussed above. They form an array
388 that overlaps and scatters about the depleted MORB array on the Zr/Yb versus Nb/Yb
389 plot, consistent with no subduction-related contribution of Zr. In contrast, on the
390 Ba/Yb versus Nb/Yb plot they form an array parallel to that of MORB and offset to
391 far higher Ba/Yb. This is a Type C array (Fig. 8), and contouring indicates that 96-98
392 % of Ba in these lavas is contributed by the subduction-related component.

393 Also plotted on Fig. 9 are compositional fields from the intra oceanic South
394 Sandwich and Mariana arcs. South Sandwich database consists of 1-4 analyses from
395 each of 12 different volcanoes (Pearce et al., 1995), and the Mariana database consists
396 of 1-7 analyses from each of 7 different volcanoes (Elliott et al., 1997). Both
397 represent overview studies of entire arcs rather than detailed studies of individual
398 volcanoes so in terms of what these analyses represent they are not directly
399 comparable to our Raoul data set, however the compositional ranges are of the same
400 order of magnitude as the Raoul samples. Values of Nb/Yb reveal that the mantle
401 component in South Sandwich lavas ranges from as depleted as that in Raoul lavas to
402 somewhat less depleted.

403 There is no indication of Zr in the subduction-related component for most
404 South Sandwich lavas, although up to 30 % of Zr could be subduction-related in some

405 Mariana lavas. Type C arrays are formed by South Sandwich and Mariana lavas on
406 the Ba/Yb versus Nb/Yb plot, and the subduction-related contribution for Ba ranges
407 from 96 % (South Sandwich lavas) to 98 % (Mariana lavas).

408 Raoul, South Sandwich, and Mariana lavas form Type C arrays on a plot of
409 Th/Yb versus Nb/Yb (Fig. 9). For Raoul lavas, the subduction-related contribution of
410 Th ranges from a minimum of 80 % to a maximum of 90 %, and this range in Th/Yb
411 occurs at both high and low Nb/Yb. South Sandwich and Mariana lavas tend to have
412 higher subduction-related contributions for Th (up to 94 %), and both average 90 %.
413 On Ba/Yb versus Nb/Yb and Th/Yb versus Nb/Yb plots Raoul lavas form arrays that
414 indicate subduction-related contributions for Ba and Th of 96-98% and 80-90 %
415 respectively added to the depleted mantle before near-fractional melting of the mix. If
416 near-fractional melting generated the array on these plots, and the consistent
417 development of Type C arrays rather than Type B arrays on X/Yb versus Nb/Yb plots
418 provides strong evidence that this was so, then some additional component
419 replenished Ba in the melting column as it ascended. This component is inferred to be
420 the aqueous LILE-bearing fluid.

421 The arrays formed on a plot of Sr/Yb versus Nb/Yb (Fig. 9) are more
422 scattered, reflecting strong partitioning of Sr into plagioclase. For Raoul, three of four
423 representative aphyric lavas with 52-56 wt.% SiO₂ plot in the middle of the Sr/Yb
424 versus Nb/Yb array, and 70-80 % of their Sr is subduction-related. The other aphyric
425 lava has 57.8 wt.% SiO and the lowest Sr/Yb value, probably as a result of extensive
426 plagioclase fractionation. Conversely, two basaltic slightly porphyritic lavas with 20-
427 30 % modal plagioclase and 15 % modal augite have the highest Sr/Yb values,
428 demonstrating the effect of plagioclase accumulation. The obliquity of the South
429 Sandwich array relative to the MORB array on Fig.9 suggests a strong plagioclase

430 fractionation effect, and these arrays are not oblique on the fractionation-corrected
431 plot presented by Pearce et al. (1995). In contrast, most Mariana analyses do not
432 appear strongly affected.

433 In summary, Raoul, South Sandwich, and Mariana lavas form Type C arrays
434 on plots of X/Yb versus Nb/Yb, where X is Nd, La, K, Pb, Rb, or Cs and a review of
435 the subduction-related contribution for Zr, Nd, La, Sr, Th, K, Pb, Rb, Ba, and Cs is
436 given in Table 3. A surprising feature is the consistent magnitude of the subduction-
437 related contribution for each element in each of these arcs. Furthermore, few elements
438 differentiate between Raoul, South Sandwich, and Mariana lavas; the largest
439 difference occurs for Ba. This difference is sufficient to separate their arrays on the
440 Ba/Yb versus Nb/Yb plot (Fig. 9). A more subtle difference is apparent for Th, and
441 for this element the subduction-related contribution in Raoul lavas is slightly less than
442 that for South Sandwich and Mariana lavas (Fig. 9).

443 The compositional arrays displayed by Raoul lavas in Fig. 8 are interpreted as
444 the result of addition of a subduction-related component which is of essentially
445 constant composition and magnitude to a depleted mantle which is also of essentially
446 constant composition (e.g. Abe et al., 1998), followed by near-fractional melting of
447 the mix. Lavas from the South Sandwich and Mariana arcs form comparable arrays,
448 and their subduction-related component is almost indistinguishable from that in Raoul
449 lavas. However, the mantle beneath some South Sandwich volcanoes is less depleted,
450 and that beneath the Mariana arc is consistently less depleted.

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454 **4. Discussion of the fractional melting model**

455 Further insights into subduction-related magma genesis can be gained from
456 plots of X/Z versus Nb/Yb, where X and Z are incompatible elements. If the
457 contributions of both slab and mantle are essentially constant then early melts
458 generated by near-fractional melting will have relatively high X/Z and high Nb/Yb for
459 $D_x < D_z$. Later melts from the depleted melting column will have relatively low X/Z
460 and low Nb/Yb. Analyzed lavas will then form an array of positive slope on a plot of
461 X/Z versus Nb/Yb (i.e., increasing X/Z with increasing Nb/Yb), so long as melt
462 pooling and mingling does not obliterate the signature of individual melt batches. In
463 contrast, a scattergram with random trend will result if either component is of variable
464 composition or if they are mixed in varying proportions. The array slope will be
465 negative if $D_x > D_z$ and the order of increasing D for the elements of interest during
466 melting of a spinel lherzolite is taken to be Cs ~ Rb ~ Ba < Th < Nb ~ K < La < Pb < Sr
467 < Nd < Zr << Yb (Sun and McDonough, 1989).

468 Raoul lavas form an array with a slight negative slope on a plot of Ba/Rb
469 versus Nb/Yb (Fig. 10) as expected, because D_{Ba} is slightly greater than D_{Rb} (Sun
470 and McDonough, 1989). Arrays for South Sandwich and Mariana lavas are sub-
471 parallel to that for Raoul. The Mariana array is displaced to higher Nb/Yb, whereas
472 the South Sandwich array is displaced to lower Ba/Rb. A comparable result is
473 obtained from a plot of Ba/Pb versus Nb/Yb (Fig. 10). The main difference between
474 these plots is that array slopes for Ba/Pb versus Nb/Yb are positive because $D_{Ba} < D_{Pb}$
475 (Sun and McDonough, 1989). Values of Ba/Pb for the Raoul, South Sandwich, and
476 Mariana arrays are more scattered than for Ba/Rb, and Ba/Pb is slightly higher for
477 Raoul and the Mariana arrays relative to the South Sandwich array. Nevertheless,
478 both the Ba/Rb versus Nb/Yb and Ba/Pb versus Nb/Yb plots are consistent with near-

479 fractional melting of an initially homogeneous source composition. Predicted array
480 patterns are also obtained for plots of Ba/Cs, Ba/K Ba/La, and Ba/Sr versus Nb/Yb
481 (not shown).

482 Very different behavior is apparent on a plot of Ba/Th versus Nb/Yb (Fig. 10)
483 where Raoul lavas form a well-defined array with negative slope South Sandwich and
484 Mariana lavas also form arrays with negative slope. The South Sandwich array is
485 offset to lower Ba/Th, and the Mariana array is offset to higher Ba/Th. However, D_{Ba}
486 $< D_{Th}$ (Sun and McDonough, 1989) therefore, the array slope should be positive. The
487 LILE are strongly partitioned into the aqueous fluids released during dehydration of
488 amphibole or serpentinite in the subducting slab and in general terms these elements
489 are partitioned into the fluid phase in proportion to their ionic radius. (Tatsumi et al.,
490 1986; Brenan et al., 1995; Keppler, 1996). Thus, both Th and U are expected to be
491 less mobile in the fluid phase than Ba and other LILE. Both theoretical and
492 experimental studies suggest that the solubility of Th in slab-derived aqueous fluids
493 will be less than, or at most equal to (if garnet is a residual phase in the slab), that of
494 U (Bailey and Ragnarsdottir, 1994; Brenan et al., 1995; Keppler, 1996). Isotopic
495 disequilibrium in the U-Th decay series requires at least two distinct subduction-
496 related components in intra-oceanic arc lavas one with high Ba/Nb associated with a
497 large $^{238}\text{U}/^{230}\text{Th}$ excess, and one with high Th/Nb and no ^{238}U excess (Elliott et al.,
498 1997). Regional studies of volcanic arcs also reveal a correlation of high Ba/Th with
499 low $^{87}\text{Sr}/^{86}\text{Sr}$ and low Ba/Th with high $^{87}\text{Sr}/^{86}\text{Sr}$ (Hawkesworth et al., 1997). These
500 observations lead to the conclusion that the LILE and Th are transferred from the
501 subducting slab by different mechanisms, and that their source reservoirs are distinct.
502 The LILE are thought to be rapidly transported by an aqueous fluid, whereas Th

503 resides in subducting sediment and may migrate in a siliceous melt (Elliott et al., 1997
504 Hawkesworth et al., 1997).

505 Other explanations for the Ba/Th trend are possible. For example, the
506 geochemical signature of the subduction-related component should be clearest in
507 lavas with a strongly depleted mantle component (e.g., Hawkesworth and Ellam,
508 1989). If decreasing Nb/Yb is taken as evidence of mantle depletion, then lavas with
509 low Nb/Yb might be assumed to better represent element ratios in the subduction-
510 related component. The plot of Ba/Th versus Nb/Yb could then lead to the conclusion
511 that the subduction-related component in Raoul lavas has $Ba/Th > 700$. However, this
512 line of reasoning cannot be valid because it implies the subduction-related component
513 is added to a variably depleted mantle component. That would generate Type B arrays
514 for Raoul lavas on X/Yb versus Nb/Yb plots, not the Type C arrays observed. Thus,
515 the Type C arrays for Raoul lavas require that any interpretation of X/Z versus Nb/Yb
516 plots reflect near-fractional melting about a mantle component of constant
517 composition.

518 This geochemical evidence leads to the conclusion that the subduction-related
519 component and the mantle-derived component are mixed in constant proportions, and
520 this mixing process presumably initiates the melting column. Increases in Ba/Th
521 during melting are attributed to continual minor inputs of a LILE-bearing fluid into
522 the melting column. The model can be tested. One prediction is that Ba/Z will
523 increase with decreasing Nb/Yb so long as Z is a conservative element, or any
524 element not present in the LILE-bearing fluid. An appropriate plot is Ba/Nb versus
525 Nb/Yb. No continual addition of LILE will yield a positive slope for the Raoul array
526 on this plot, as $D_{Ba} < D_{Nb}$ (Sun and McDonough, 1989). The negative slope on Ba/Nb

527 versus Nb/Yb (Fig. 10). indicate the continual input of a LILE-bearing component to
528 the melting column.

529 Predicted array slopes on plots of Ba/Z versus Nb/Yb depend upon D values.
530 Partition coefficients for D_{Ba} cited by Ewart et al. (1998), are $D_{Ba} > D_{Th}$ and $D_{Ba} >$
531 D_{Nb} although these relatively high values are at variance with other data compilations
532 (e.g., Sun and McDonough, 1989; McCulloch and Gamble, 1991; Stolper and
533 Newman, 1994). Published databases concur that $D_{Rb} < D_{Th}$ and $D_{Cs} < D_{Th}$ during
534 mantle melting (Sun and McDonough, 1989; McCulloch and Gamble, 1991; Stolper
535 and Newman, 1994; Ayres et al., 1997; Ewart et al., 1998; Ayres, 1998). Raoul lavas
536 form arrays of negative slope on plots of Rb/Th versus Nb/Yb and Cs/Th versus
537 Nb/Yb, although with appreciable scatter. Therefore, replenishment of both Rb and Cs
538 relative to Th is also required in the ascending melting column, supporting the
539 evidence provided by changes in Ba/Th.

540 A further test is provided by changes in radiogenic isotope ratios with Nb/Yb.
541 None of the analyzed radiogenic isotopes ($^{87}/_{86}Sr$, $^{143}/_{144}Nd$, $^{206}/_{204}Pb$, $^{207}/_{204}Pb$,
542 $^{208}/_{204}Pb$) show any correlation with SiO_2 or other major or trace element
543 concentrations in Raoul lavas. However, Raoul lavas form an array with negative
544 slope on a plot of $^{87}/_{86}Sr$ versus Nb/Yb (Fig 11). The higher $^{87}/_{86}Sr$ values of lavas
545 with low Nb/Yb, which are those melts generated at a relatively late stage from the
546 melting column, is best explained by the continual addition of a small amount of
547 LILE-bearing fluid with high $^{87}/_{86}Sr$ to the melting column. The South Sandwich
548 array also has a negative slope for $^{87}/_{86}Sr$ versus Nb/Yb. Other analyzed radiogenic
549 isotopes do not show significant correlations with Nb/Yb, although the slope of the
550 Raoul array for $^{206}/_{204}Pb$ versus Nb/Yb is slightly positive (Fig. 11).

551 In conclusion, the geochemical arrays formed by Raoul lavas on plots of X/Z
552 versus Nb/Yb are best interpreted in terms of a near-fractional melting model. These
553 plots require one subduction-related component for the LILE (Sr, K, Pb, Rb, Ba, Cs)
554 and another for Th. Furthermore, they indicate continual minor addition of LILE-
555 bearing fluid to the melting column as it ascends, but no replenishment of Th (or
556 conservative elements). Higher $^{87}/_{86}\text{Sr}$ in late stage melts from the column also
557 testifies to the continual addition of a LILE-bearing fluid. Similar trends are shown by
558 South Sandwich and Mariana lavas.

559 **5. Discussion**

560 *5.1 Origin of mantle depletion*

561 Subduction-related magmas from intra-oceanic arcs with active backarc
562 basins, such as the Tonga-Kermadec arc, are characterized by a depleted mantle
563 component (Ewart and Hawkesworth, 1987; McCulloch and Gamble, 1991; Pearce
564 and Parkinson, 1993; Woodhead et al., 1993). Some conservative elements in Raoul
565 lavas are mildly depleted relative to FMM (e.g., Nb, Zr, Ti), but this depletion is
566 restricted to those elements with $D_C < D_Y$ during mantle melting. Conservative
567 elements that are highly sensitive to mantle melting and depletion events have
568 concentrations consistent with the generation of Raoul primary magmas by 15-35 %
569 melting of FMM from which a melt fraction of up to 4 % has previously been
570 extracted. However, Raoul lavas form Type C arrays on plots of X/Yb versus Nb/Yb.
571 Such arrays indicate near-fractional melting of a homogeneous source, and cannot
572 ordinarily be produced by melting of variably depleted mantle mixed with a
573 subduction-related component.

574 These observations can be reconciled by re-interpreting mantle melting and
575 depletion in terms of a near-fractional melting process from which early formed melts
576 have high Nb and Yb in contrast with later melts from the melting column which will
577 have relatively low Nb and Yb. The dimensions of the Raoul array on Fig. 6 are thus
578 an artefact of fractional melting about a mid point composition. The true mantle
579 composition is FMM from which a ~2 % melt fraction has previously been extracted.
580 Similarly, the range in Nb/Yb of 0.13-0.33 is interpreted as an artefact of fractional
581 melting about a homogeneous source with average Nb/Yb of 0.22 (e.g., Type C
582 behaviour on fig 8), this compares with a MORB Nb/Yb of 0.76 (Pearce and
583 Parkinson, 1993).

584 The origin of mantle depletion beneath intra-oceanic arcs has been much
585 discussed (e.g., Ewart and Hawkesworth, 1987; McCulloch and Gamble, 1991; Pearce
586 and Parkinson, 1993; Woodhead et al., 1993; Elliott et al., 1997). Potentially, mantle
587 depletion may occur by:

- 588 1) progressive melt extraction from sub-arc mantle, coupled with minimal
589 advection of fresh material into the sub-arc zone.
- 590 2) melt extraction from a melting column beneath the spreading centre of a
591 backarc basin, followed by advection of depleted mantle into the sub-arc zone.
- 592 3) recycling of depleted mantle residue from the sub-arc melting column through
593 the mantle wedge and back into the melting column.
- 594 4) continual loss of early formed melts from the base of the sub-arc melting
595 column.

596 There is a general consensus that (2) is the dominant process, and this is strongly
597 supported by the occurrence of undepleted or enriched mantle components in
598 subduction-related magmas from intra-oceanic arcs that lack active backarc basins,

599 such as the West Aleutian and Vanuatu arcs. Some consider (4) may also be
600 significant (Pearce and Peate, 1995).

601 Key conclusions reached for the mantle component in Raoul lavas are that the
602 degree of depletion is minor and of constant magnitude with time. These are
603 inconsistent with (1), in which mantle depletion would increase with time, and with
604 (3), in which variable and random mantle depletion with time is more likely. Instead,
605 the rate of mantle advection must be sufficient that a new unit of homogeneous mildly
606 depleted mantle replenishes the base of the melting column for each unit that begins
607 to melt and ascend.

608 The generation of homogeneous mildly depleted mantle beneath a backarc
609 spreading centre is not problematic. Trace element concentrations in the
610 clinopyroxene of abyssal peridotites (mantle residue) indicate that small melt fractions
611 (0.1-1.0 %) readily segregate from mantle melting columns (Johnson et al., 1990).
612 Thus, melt extraction beneath a back arc spreading centre produces a homogeneous
613 depleted residue. The extent of depletion will depend upon the average height to
614 which the melting column ascends (extent of decompression) and its temperature
615 (Klein and Langmuir, 1987; McKenzie and Bickle, 1988). If the rate of mantle
616 advection is driven by the down-drag of mantle adjacent to the subducting slab (e.g.,
617 Davies and Stevenson, 1992), and spreading centers beneath active backarc basins
618 represent passive mantle upwelling, then it is reasonable to expect a relationship
619 between the rate of backarc extension and mantle depletion because faster extension
620 at a fixed subduction rate will allow mantle in the backarc basin melting column to
621 rise higher and undergo more melting before it is advected out of that column and
622 towards the sub-arc melting column.

623 Subduction rates beneath Raoul and the South Sandwich and central Mariana arcs
624 are essentially identical, whereas backarc extension rates vary (Table 4). Taking
625 Nb/Yb as an indicator of mantle depletion, Raoul has the most depleted mantle
626 composition and the lowest backarc extension rate. Comparable subduction and
627 backarc extension rates for Raoul and the central Mariana arc should result in
628 similarly depleted mantle components, but Raoul lavas [average Nb/Yb = 0.22] are
629 markedly more depleted than those of the Mariana arc [average Nb/Yb = 0.49]. Some
630 of this difference arises from the comparison of data from a single volcano (Raoul)
631 with databases consisting of few analyses from many volcanoes (South Sandwich and
632 Mariana).

633 In summary, the sub-arc mantle beneath Raoul is required to be homogeneous and
634 to advect rapidly into the sub-arc melting column in order to avoid the development of
635 a long term depletion trend, and to be mildly depleted with respect to FMM (Nb/Yb =
636 0.22). A comparison with lavas from the intra-oceanic South Sandwich and Mariana
637 arcs reveals no obvious link between the degree of mantle depletion and the
638 subduction rate, backarc extension rate, or backarc basin width. We suggest that
639 further sampling of the Tonga-Kermadec arc and modelling of geochemical analyses
640 in terms of near-fractional melting will provide the means to unlock this puzzle. In
641 particular, the middle section of the arcs (from L'Esperance Rock to 'Ata Island)
642 provides an opportunity to examine conservative element co-variations as from south
643 to north the backarc extension half-rate increases from 1.9 to 6.5 cm per year and the
644 subduction rate increases from 7.2 to 13.5 cm per year, the latter predominantly in
645 response to the higher rate of backarc extension. The mantle composition has Pacific
646 MORB-source affinities throughout this part of the arc (Smith and Price, 2006 and
647 references therein).

648 *5.2 Buffering of the subduction-related component*

649 The distinctive high LILE/HFSE ratios of subduction-related magmas compared with
650 MORB are generally attributed to the transfer of a hydrous LILE-bearing component
651 from the subducting slab to the overlying mantle (e.g., Tatsumi et al., 1986;
652 McCulloch and Gamble, 1991; Pearce and Peate, 1995). The relative proportion of
653 each element contributed by the subduction-related component can be assessed from
654 plots of X/Yb versus Nb/Yb, where X is an incompatible element. Negligible Zr, 30
655 % of the Nd, 55 % of the La, 75 % of the Sr, 85 % of the Th, and >90 % of the K, Pb,
656 Rb, Ba, and Cs in Raoul lavas is subduction-related. Furthermore, the arrays
657 generated on these plots are consistently parallel to the MORB array and offset from it
658 by a constant proportion to higher X/Yb. Arrays of this type require tight coupling
659 between X/Yb and Nb/Yb which, except under extraordinary circumstances, can only
660 be provided by the relative distribution during mantle melting. Therefore, they
661 indicate a constant subduction-related component added to a constant mantle
662 composition, followed by near-fractional melting of the mix (Pearce et al., 1995).

663 Sources of the subduction-related component are the altered oceanic crust of
664 the subducting slab and its overlying sediment veneer. Fluids or melts generated in
665 either of these are likely to have distinct compositions that vary with depth of origin
666 within each source, and with the PT conditions of the slab. Thus, some mechanism
667 must exist to transform part (or all) of the slab-derived flux into a homogeneous
668 subduction-related component as it migrates from the slab-mantle interface to the base
669 of the melting column. Fluid (or melt) passing through the mantle will react with it to
670 attain chemical equilibrium. Two possible types of reactions are considered.

671 In the first, the interaction is analogous to the operation of a chromatographic
672 column (Navon and Stolper, 1987; Hawkesworth et al., 1994). Elements in the fluid

673 (or melt) migrate through the mantle chromatograph at rates inversely proportional to
674 their bulk mantle-fluid partition coefficients. Because the mantle is advecting, there is
675 a critical value for this parameter such that elements with distribution coefficients less
676 than the critical value do not exit the chromatograph before advection carries them
677 beyond the sub-arc melting column. These elements remain within the mantle,
678 whereas the others exit as the subduction-related component. However, the rate of
679 element migration through the chromatograph is not concentration dependent and
680 therefore, this mechanism is incapable of buffering the composition of the subduction-
681 related component in real-time. Slab-derived elements either exit the chromatograph
682 at the base of the melting column if their distribution coefficient is less than the
683 critical value or else they do not. Temporal changes in the slab-derived flux as it
684 enters the chromatograph are preserved in element concentration profiles at the exit
685 point, although element-element ratios are decoupled.

686 A second type of interaction features fluid (or melt) reacting with mantle
687 peridotite to form amphibole (Tatsumi et al., 1986; Davies and Bickle, 1991; Davies
688 and Stevenson, 1992).). Mantle advection carries this metasomatised peridotite
689 formed adjacent to the subducting slab to progressively deeper levels until amphibole
690 decomposes at 3.0 GPa. An aqueous fluid (or melt if $T > 1000\text{ }^{\circ}\text{C}$), is released and
691 ascends vertically until it reaches amphibole-undersaturated mantle at lower pressure,
692 whereupon fluid (or melt) reacts with peridotite to form new amphibole. The process
693 repeats until the PT conditions of the amphibole- saturated peridotite solidus are
694 reached at the base of the sub-arc melting column (3.0 GPa, 1150°C). The
695 composition of the fluid (or melt) is controlled by the number of cycles in which
696 amphibole decomposes to pyroxene. Therefore, slab-derived material transported by
697 this process should reflect D_{pyroxene} when it reaches the melting column.

698 Recent experiments indicate that clinopyroxene distribution coefficients in
699 alkali chloride-rich fluids increases in the sequence La < Sr < Th < Pb < K < Ba < Rb,
700 and $D_{La} \sim 1$ at 0.3 GPa and 1040 °C (Keppler, 1996; Kessel et al., 2005). This
701 sequence closely resembles that of the increasing subduction-related contribution in
702 Raoul lavas of La < Sr < Th < K < Pb < Rb < Ba. Increasing pressure from 0.3 to 2.0
703 GPa changes D by less than an order of magnitude, but further experiments are
704 needed to assess the dependence of the element sequence on pressure, fO_2 , and
705 chloride concentration (Keppler, 1996). Combined amphibole-fluid (melt) transport
706 from the mantle-slab interface to the melting column appears to be the most likely
707 mechanism by which the slab-derived flux is converted to the homogeneous
708 subduction-related component mixed with the mantle at the base of the melting
709 column beneath Raoul.

710 The remarkable similarity between the subduction-related contribution for
711 Raoul and that for the South Sandwich and Mariana arcs is consistent with buffering
712 of the slab-derived flux by pyroxene distribution coefficients beneath these arcs
713 However, subtle differences do exist. Chief amongst these is the Ba-rich nature of
714 Raoul and Mariana lavas relative to those of the South Sandwich arc (Fig.9). This is
715 of sufficient magnitude that their arrays are just separated on plots of Ba/Yb versus
716 Nb/Yb and Ba/Z versus Nb/Yb, where Z is any incompatible element. Raoul and
717 Mariana lavas are also slightly Th-poor relative to South Sandwich lavas and Mariana
718 lavas are richer in Zr and the REE than either Raoul or South Sandwich lavas (Fig 9).

719 There are differences in the character of the subducting slab beneath Raoul
720 and the South Sandwich and Mariana arcs. Altered oceanic crust subducting beneath
721 Raoul and the Mariana arc is of comparable age, whereas that subducting beneath the
722 South Sandwich arc is appreciably younger (Table 5). Nonetheless, hydrothermal

723 alteration of oceanic crust is most rapid at mid-ocean ridges, is completed in <70 Ma,
724 and is probably independent of the spreading rate (e.g., Stein and Stein, 1994; German
725 et al., 1995). Therefore, inter-arc changes in the fluid or melt flux emanating from
726 subducting oceanic crust are not expected. Major inter-arc differences occur in the
727 thickness and composition of subducting sediments (Table 5). Two estimates of the
728 sediment flux beneath Raoul have been calculated. One utilises the average
729 composition of sediment from DSDP 204 (100 km east of Tonga), and the other that
730 from DSDP 595/596 (950 km east of Tonga). The calculated fluxes differ markedly
731 (e.g., $Ba_{flux}/Th_{flux} = 52-173$, $Ba_{flux}/Rb_{flux} = 7-43$), and typically bracket those of the
732 South Sandwich and Mariana arcs.

733 In summary, the main subduction-related contribution in Raoul lavas is of
734 constant composition and magnitude. This is consistent with material derived from the
735 subducting oceanic crust and its sediment veneer being transported from the slab-
736 mantle interface to the base of the sub-arc melting column by alternating episodes of
737 amphibole formation and amphibole decomposition to pyroxene with fluid release,
738 leading to further amphibole formation. The composition of the subduction-related
739 component reaching the melting column is thus buffered by pyroxene distribution
740 coefficients. Subtle differences in the subduction-related contribution between Raoul
741 and the South Sandwich and Mariana arcs resemble changes in the bulk composition
742 of subducting sediment, but sediment compositions are poorly constrained.

743 *5.3 Role of amphibole-saturated peridotite*

744 The co-variation of X/Yb with Nb/Yb, where X is an incompatible element
745 leads to the conclusion that magma genesis beneath Raoul involves near- fractional
746 melting of mildly depleted mantle mixed with a subduction-related component.
747 Neither component varies significantly in composition through the exposed sequence

748 on Raoul Volcano. In addition, both components must be mixed in set proportions for
749 Type C arrays to develop in preference to Type A arrays (Fig. 8). Thus, upwelling of
750 the melting column is apparently initiated by the addition of a fixed amount of the
751 subduction-related component to the mantle.

752 This constraint is difficult to explain if slab-derived fluid or melt migrates
753 freely from the slab-mantle interface to the base of the melting column, or by
754 chromatographic exchange reactions. Temporal changes in the flux of H₂O and other
755 elements, reflecting heterogeneity in the subducting slab, would be a reasonable
756 expectation in both cases. However, a very different outcome arises if the slab-derived
757 flux is transported to the base of the melting column by amphibole.

758 Mantle peridotite in the wedge reacts with fluid (or melt) from the subducting
759 slab until amphibole-saturation is attained (Tatsumi et al., 1986; Davies and Bickle,
760 1991; Davies and Stevenson, 1992). Excess fluid (or melt) will ascend until it reaches
761 amphibole-undersaturated mantle. Amphibole is repeatedly decomposed when down-
762 dragged to 3.0 GPa, releasing a fluid or melt, and subsequently re-formed at lower
763 pressures.. Eventually, amphibole decomposition occurs at the PT conditions that
764 mark the amphibole-saturated peridotite solidus and define the base of the sub-arc
765 melting column (3.0 GPa, 1150 °C). If sufficient fluid is transferred from the slab,
766 then all mantle peridotite passing through the base of the melting column will be
767 amphibole-saturated and contain a fixed modal proportion of amphibole. This is
768 equivalent to a fixed unit of the subduction-related component mixed with a fixed unit
769 of the mantle. Furthermore, this amphibole-saturated peridotite will have a fixed H₂O
770 content, and the composition of the subduction-related component will be buffered by
771 pyroxene distribution coefficients

772 Our observations and calculations indicate that in this model a 2-8 % melt
773 fraction is generated at the amphibole-saturated solidus, with 1.6-6.0 wt.% H₂O in the
774 melt (Davies and Bickle, 1991). The H₂O content in this initial melt fraction is
775 significantly greater than that estimated for primitive subduction-related magmas of 2-
776 4 wt.% H₂O (Davies and Stevenson, 1992; Sisson and Grove, 1993). Decompression
777 melting of MORB source mantle results in up to 18 % melting for long melting
778 columns (Kinzler and Grove, 1992). By analogy, this will augment the initial melt
779 formed at the base of the sub-arc melting column and dilute its H₂O content. A
780 magma may also exsolve H₂O as it rises (e.g., Sisson and Grove, 1993).

781 We suggest that excess H₂O in the initial melt may play another role. Plots of
782 X/Z versus Nb/Yb, where X and Z are incompatible elements, indicate continued
783 replenishment of the melting column by a LILE-rich component. This component is
784 of small magnitude relative to the total subduction-related component. Potentially,
785 aqueous fluid released during amphibole decomposition at the base of the sub-arc
786 melting column exceeds H₂O saturation of the melt. An aqueous fluid with the
787 composition of the subduction-related component could then exist as a free phase, and
788 percolate to higher levels until encountering H₂O undersaturated conditions within the
789 mantle-melt mix. The rapid upwards percolation of a free aqueous phase may be
790 important in the development of U-Th isotopic disequilibrium, which require a very
791 short transit time of 30-120 ka. for U and other LILE from the subducting slab to
792 eruption (Hawkesworth et al., 1997).

793

794 **6. Conclusion**

795 The genesis of magmas in subduction zones is ultimately the result of the
796 interaction of recycled oceanic crust and the overlying mantle wedge. The product of
797 this interaction is primitive arc-type magma although because of crustal processes this
798 is typically profoundly modified in its passage toward the surface (eg Price et al.,
799 2005). In this paper we have used the variation in trace element abundances in a
800 single magmatic system to assess the relative contribution of different components to
801 magma genesis in a simple tectonic setting where evolved continental crust is absent.

802 Key findings are that:

- 803 1. Magmas are produced within the mantle wedge by near fractional
804 melting triggered by the release of fluids at the amphibole breakdown
805 point. For Raoul Volcano this source is depleted in incompatible
806 elements by about 2% relative to fertile MORB mantle.
- 807 2. A subduction-related component of constant composition and
808 magnitude has been added to this mantle source. A homogeneous
809 subduction-related component of constant composition and magnitude
810 is produced if the slab-derived fluid flux migrated into the slab-mantle
811 interface to the sub-arc melting column by repeated episodes of
812 amphibole formation and decomposition and its composition is then
813 governed by pyroxene distribution coefficients. The remarkably
814 similar composition and magnitude of the subduction-related
815 component in Raoul, South Sandwich and Mariana lavas despite
816 variations in subducting sediment flux testifies to the buffering effect
817 of this transfer mechanism.

818 3. A second and more mobile LILE-bearing component is continuously
819 added to the melt column and this is also responsible for higher
820 ⁸⁷/₈₆Sr. Similar trends are shown by South Sandwich and Mariana
821 lavas.

822

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1002

1003 **Appendix 1. Analytical methods**

1004 Samples were washed and dried to remove possible sea-spray contamination and
1005 crushed in a tungsten carbide ring grinder. H_2O^- and loss on ignition (LOI) were
1006 determined by weight loss after heating to 115°C and 950°C respectively. Major
1007 elements were analyzed using fused glass discs (La-doped lithium tetra borate/ lithium
1008 metaborate flux) by X-ray Fluorescence at University of Auckland (Phillips PW1410
1009 wavelength-dispersive spectrometer) using standard matrix correction procedures. For
1010 a typical Raoul lava the precision (1σ) of the major elements is better than 0.5% for
1011 SiO_2 , 0.5-1.0 % for TiO_2 , Al_2O_3 , Fe_2O_3 and CaO , 1-3% for MgO , Na_2O and K_2O and
1012 308% for MnO and P_2O_5 .

1013

1014 Minor trace elements were analyzed in solution at Monash University using the VG
1015 Plasmaquad PQ2⁺ spectrometer. Sample preparation involved digesting in an HF-

1016 HNO₃ mix, evaporating to dryness, refluxing twice in concentrated HNO₃ before
1017 taking up in 50 ml of 2% HNO₃ for a final dilution factor of approximately 2000. ¹¹⁵In
1018 was used as an internal standard. The precision (1σ) is 4-7% for REE, Hf and Pb, 7-
1019 12% for Ge, Rb, Nb, Cs, Ta, Th and U, and 1-4% for the remainder. Detection limits
1020 are less than ~10ppb. The precision of each analysis was provided by VIEPS (Victoria
1021 Institute of Earth and Planetary Science) in-run standard deviation/average analysis.

1022

1023 Isotopic analyses were analyzed by thermal ionization mass spectrometry. Samples
1024 were leached in 4 ml of 5.25N HNO₃ and rinsed with deionised water to guarantee no
1025 residual contamination from sea spray. The leached sample was digested in 2 ml of
1026 40% HF and evaporates to dryness; this step was repeated. A further 1 ml of 40% HF
1027 combined with 2 ml concentrated HNO₃ was added and evaporated at 110°C until
1028 dissolution was complete and the solution was then divided equally into a Sr+Nd and
1029 a Pb split before evaporation to dryness. The Sr+Nd split was redissolved in 2 ml of
1030 1N HCl and cation chromatography used to generate Sr and Nd concentrates. The Pb
1031 split was redissolved in 1N HCl and Pb extracted using conventional HBr-HCl
1032 column chemistry. All Sr, Nd, and Pb isotope ratios were analyzed using the
1033 Finnegan-MAT 262 multicollector mass spectrometer at La Trobe University. Three
1034 Sr-Nd and four Pb procedural blanks were analysed, these reported Sr < 2 ng, Nd < 50pg
1035 and Pb < 0.8 ng. No blank corrections have been applied as the blank levels were
1036 negligible relative to the sample sizes used. During the course of this analytical work
1037 NBS987 reported ⁸⁶/₈₇Sr ratios = 0.71024 ± 0.00003 (n=7) compared to a long term
1038 laboratory average of 0.71024 ± 0.00004 and an accepted ratio of 0.71024. Repeated
1039 analysis of La Jolla reported ¹⁴³/₁₄₄Nd = 0.511855 ± 0.000006 (n=3) compared to a
1040 long term laboratory average of 0.511857 ± 0.000002 and an accepted ratio of

1041 0.511850. For Pb the average errors in analyses of NBS981 were 0.10% for $^{206}/_{204}\text{Pb}$,
1042 0.13% for $^{207}/_{205}\text{Pb}$ and 0.18% for $^{208}/_{204}\text{Pb}$ (n=78 for the laboratory. All errors quoted
1043 are 2σ of the mean.

1044

1045 **Figure captions**

1046 1. Tectonic setting of Raoul Island vs trench and ridge. The active and remnant
1047 arcs of the region and the Louisville seamount chain are defined
1048 topographically by the 2000 m bathymetric contour and the Kermadec and
1049 Tonga trenches are defined by the 7000 m bathymetric contour. TVZ signifies
1050 the Taupo Volcanic Zone of central North Island New Zealand.

1051 2. Plot of Mg# (mol.% MgO/(MgO+FeO)) against SiO₂ for all Raoul Volcano
1052 lavas. Samples with high Mg# and low SiO₂ have high phenocryst contents
1053 (40-50 vol.%) and their apparently primitive compositions reflect mafic
1054 mineral accumulation.

1055 3. Fertile MORB Mantle (FMM) source normalized plot for conservative
1056 elements in aphyric (darker shading) and slightly porphyritic (lighter shading)
1057 Raoul lavas. Elements are plotted in order of increasing D_C (distribution
1058 coefficient for conservative elements). The FMM composition, the MORB
1059 composition and the element order are taken from Pearce and Parkinson
1060 (1993). Raoul lavas are depleted in those elements more incompatible than Y
1061 relative to MORB but not for other conservative elements.

1062 4. Al₈ / Ti₈ versus Ca₈ / Ti₈ for Raoul lavas. Aphyric lavas (solid circles) plot
1063 alongside MORB and do not require re-melting of a depleted mantle source
1064 (MORB value at 7.5 wt.% MgO calculated from Pearce and Parkinson, 1993).
1065 Progressively more porphyritic lavas (open squares) plot in an array extending

1066 to higher values of both ratios. Vectors depict plagioclase, clinopyroxene, and
1067 olivine accumulation. Fields for experimental fertile and depleted mantle melts
1068 regressed to MgO = 8 wt.% (Hawaiian pyrolite and Tinaquillo lherzolite,
1069 respectively), and the Tonga-Kermadec arrays (lighter stipple uncorrected for
1070 crystal accumulation), are after Turner et al., (1997) and references therein.

1071 5. Na₈ versus Fe₈ for Raoul lavas. Aphyric lavas (solid dots) plot on an extension
1072 of the global MORB trend to low Na Fe, other lavas (open squares) plot in a
1073 scattered field consistent with modification by crystal fractionation processes.
1074 Vectors depict plagioclase, clinopyroxene, and olivine accumulation. Fields for
1075 experimental fertile and depleted mantle melts regressed to MgO = 8 wt.%
1076 (Hawaiian pyrolite and Tinaquillo lherzolite, respectively), Lau backarc basin
1077 basalt (BABB), and the Tonga-Kermadec arrays (lighter stipple uncorrected for
1078 crystal accumulation) are after Turner et al. (1997) and references therein.
1079 Global MORB trend is after Pearce et al. (1995).

1080 6. Nb versus Yb for representative Raoul lavas Most form a cluster centered on 25
1081 % melting of a source depleted by 2 % melt extraction relative to FMM (Nb
1082 and Yb analyses by ICP-MS). Three lavas plot as outliers. Calibration of the
1083 diagram, South Sandwich, Mariana, New Hebrides, and Aleutian fields after
1084 Pearce and Parkinson (1993).

1085 7. MORB normalized incompatible element plot for representative Raoul lavas.
1086 The analyses bracket the spread of MORB-normalised patterns. Element
1087 abundances increase with SiO₂, LILI are enriched and most HFSE are flat.
1088 Normalisation factors after Pearce and Parkinson (1993).

- 1089 8. Behavior of non-conservative incompatible elements in subduction zones. Four
1090 distinct trends can be generated by varying the relative inputs of mantle wedge
1091 and subducted crust. See text for further discussion.
- 1092 9. X/Yb versus Nb/Yb (where X is an incompatible element) for representative
1093 Raoul lavas (solid diamonds). Fields for South Sandwich (moderate shading
1094 data from Pearce and Peate, 1995 Pearce et al., 1995)), Mariana (cross
1095 hatching, data from Elliot et al 1997) and Ruapehu (dark shading, data from
1096 Price et al., 2005 and references therein) are shown for comparison. The
1097 MORB array and average MORB (solid dot) are also shown Dotted lines are
1098 contour lines and the amount of a subduction component is shown as a
1099 percent. The open headed arrow is an extrapolation of the Raoul array to Nb/Yb
1100 values comparable to average MORB.
- 1101 10. Plot of X/Z (Ba/Rb, Ba/Pb, Ba/Th and Ba/Nb) versus Nb/Yb. Dashed lines are
1102 arbitrary ratios of X/Z, double headed arrow is a least squares power curve
1103 fitted to the Raoul array. South Sandwich and Mariana arrays are data from
1104 Pearce et al. (1995) and Elliot et al. (1997) respectively.
- 1105 11. Plots of $^{87}/_{86}\text{Sr}$ and $^{206}/_{204}\text{Pb}$ versus Nb/Yb models invoking a constant
1106 subduction-related component, constant mantle component and a fixed ratio of
1107 mixing between these components predict horizontal arrays on both
1108 plots. Raoul lavas form an array of negative slope for Sr isotopic ratios which
1109 is best explained as resulting from continued minor input from the subduction-
1110 related component to the melting column. The array for Pb isotope ratios is
1111 horizontal within analytical error. Dashed lines are at arbitrary ratios of $^{87}/_{86}\text{Sr}$
1112 and $^{206}/_{204}\text{Pb}$ and the double-headed arrow is a least squares power curve fitted
1113 to the Raoul array. The south Sandwich array also exhibits a negative

1114 correlation between $^{87}/_{66}\text{Sr}$ and Nb/Yb. Data bases the South Sandwich and
1115 Mariana arcs are from Pearce et al (1995) and Elliot et al (1997) respectively.

1116

1117 **Tables**

1118 1. Analyses of selected representative Raoul Volcano lavas in the basalt –
1119 andesite compositional range. Aphyric lavas are indicated with an A and total
1120 phenocryst proportions are given for the other analyses. Sample numbers refer
1121 to material archived in the University of Auckland petrology collection.

1122 Analytical methods are given in the appendix.

1123 2. Equations for regressing major elements to $\text{MgO} = 8 \text{ wt.}\%$ in Raoul lavas.
1124 Each linear regression equation is of the form $Y = AX + B$, where Y is the
1125 weight proportion of the element, A is the slope, X is the MgO content, and B
1126 is the intercept. The equations were derived using 13 aphyric lava analyses
1127 only. r is the correlation coefficient for the element versus MgO.

1128 3. Subduction-related contribution of selected elements in Raoul and other lavas
1129 The average subduction-related contribution for each incompatible element is
1130 listed, and for Raoul the range is also given. Ruapehu values are those for the
1131 low-SiO₂ end of the Type D array (inferred minimal crustal assimilation).
1132 Values of Sr for Raoul are aphyric lavas only, and for South Sandwich lavas
1133 are from Pearce et al. (1995).

1134 4. Subduction, backarc extension, and Nb/Yb for Raoul and other arcs. No
1135 obvious relationship exists for subduction or backarc extension parameters
1136 with Nb/Yb for Raoul and the South Sandwich and Mariana arcs. Subduction
1137 rates, backarc extension, and backarc basin widths from Plank and Langmuir
1138 (1993), Barker (1995), Fryer (1995), and Parson and Wright (1996). Values of

1139 Nb/Yb for the South Sandwich and Mariana arcs from Pearce et al. (1995) and
1140 Elliott et al. (1997).

1141 5. Sediment flux beneath Raoul and other arcs. Sediment subduction fluxes for
1142 selected elements beneath Raoul were calculated by the method of Plank and
1143 Langmuir (1993), using average compositions for DSDP 595/596 and DSDP
1144 204 (upper 103 m only) taken from Turner et al. (1997) and assuming a
1145 density of 1.4 g/cm and H content of 40 wt.%. The South Sandwich flux was
1146 calculated from data in Ben Othman et al. (1989), whereas the Mariana flux
1147 was taken from Plank and Langmuir (1993).

Figure
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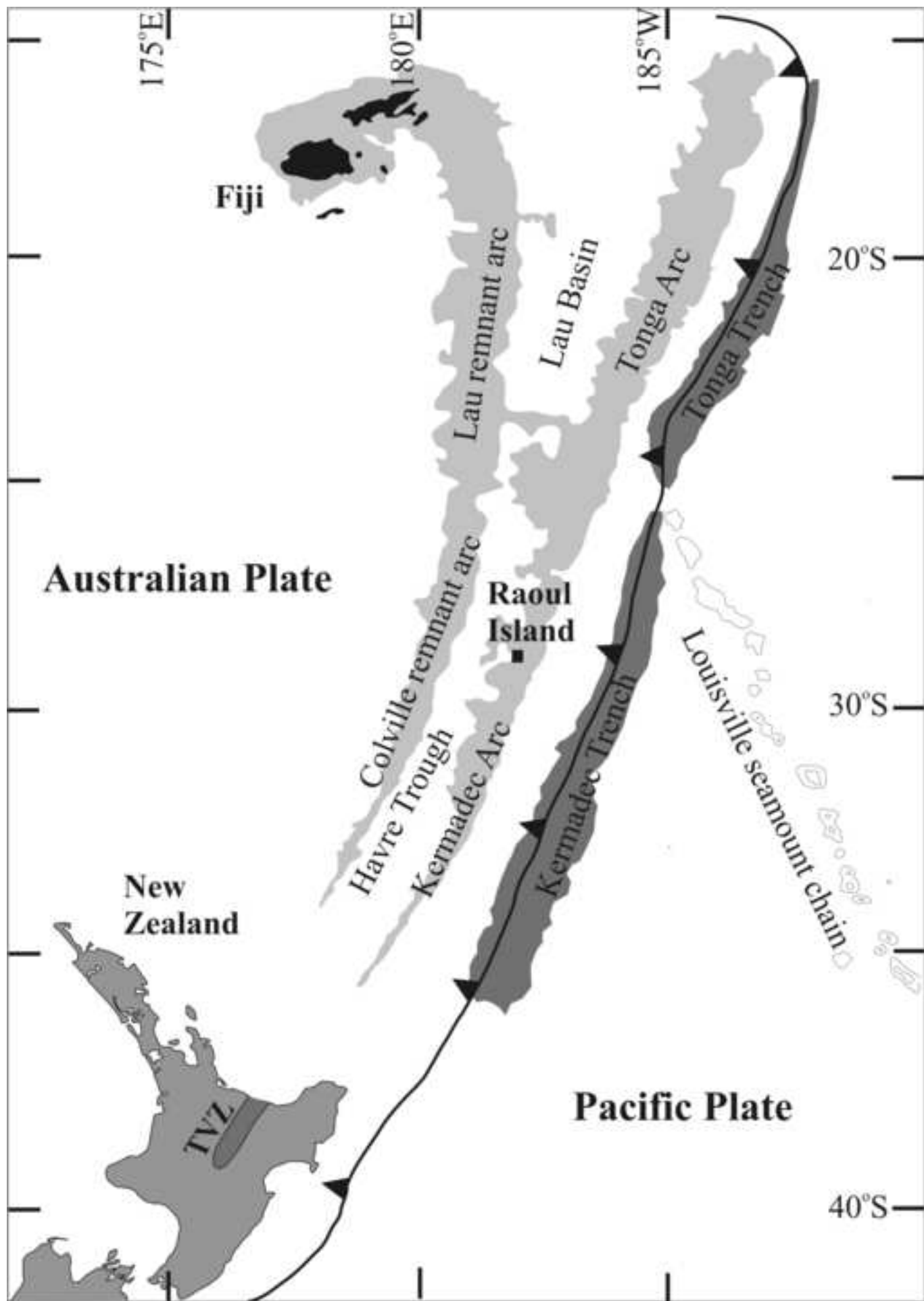


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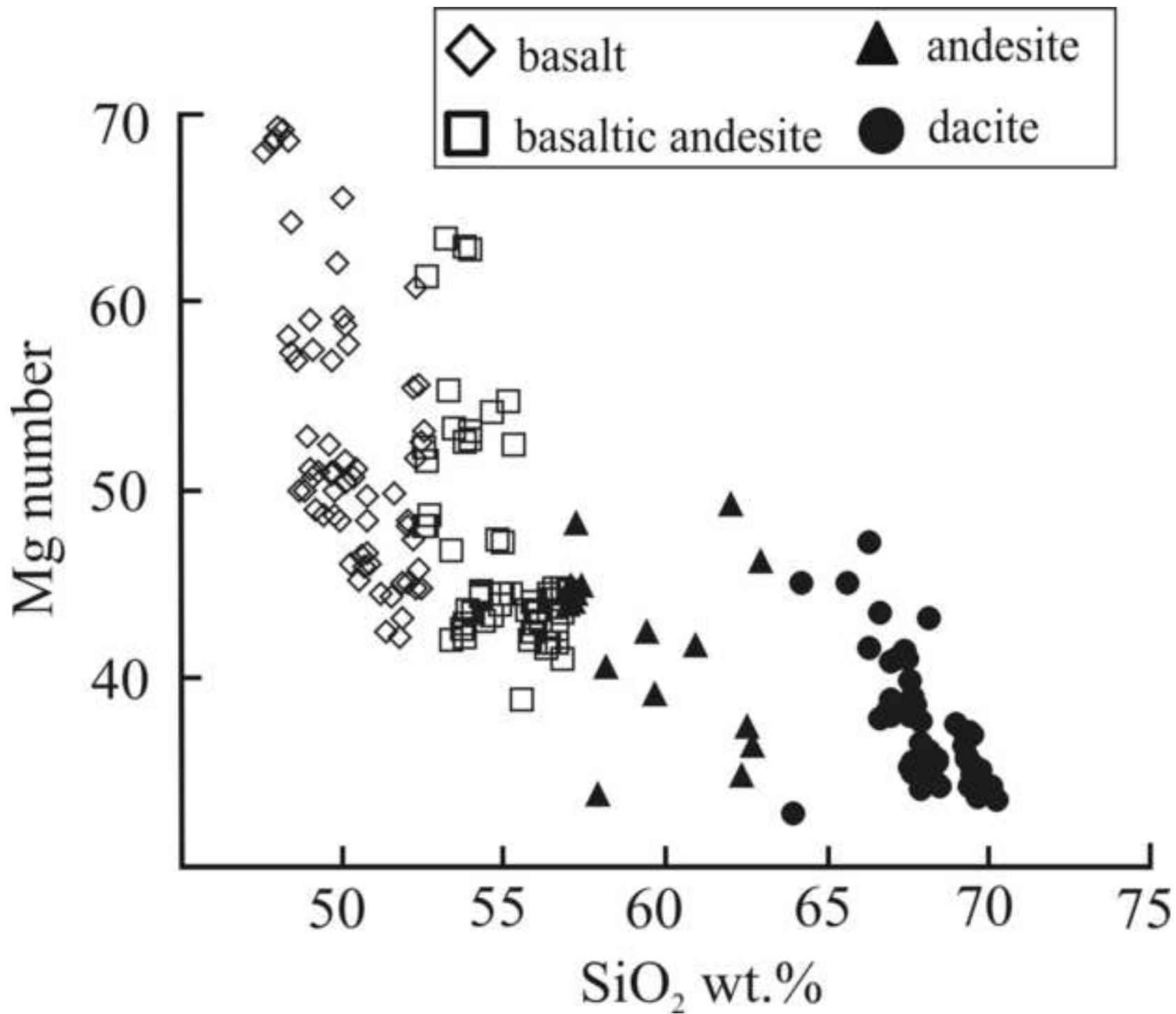


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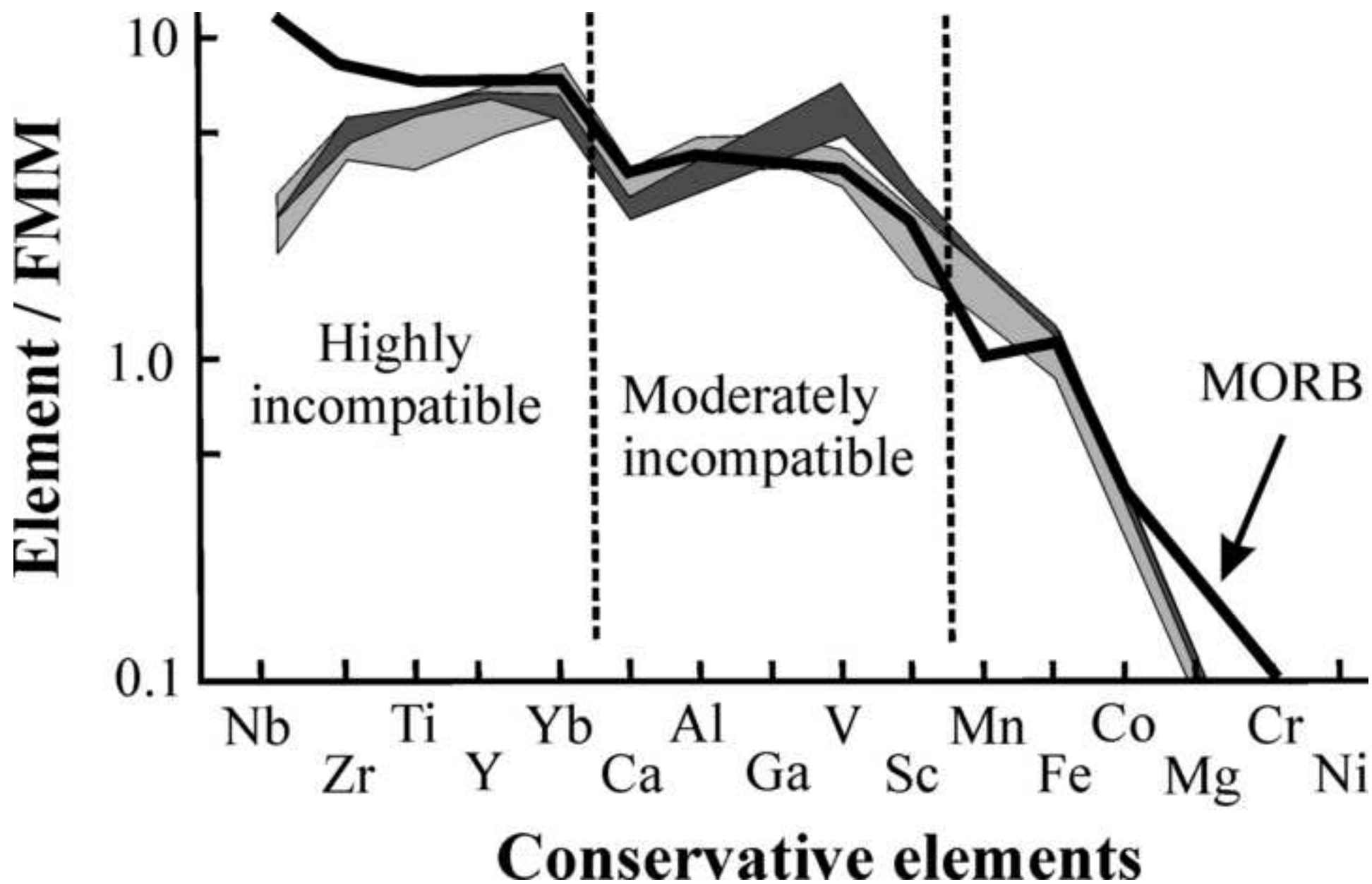


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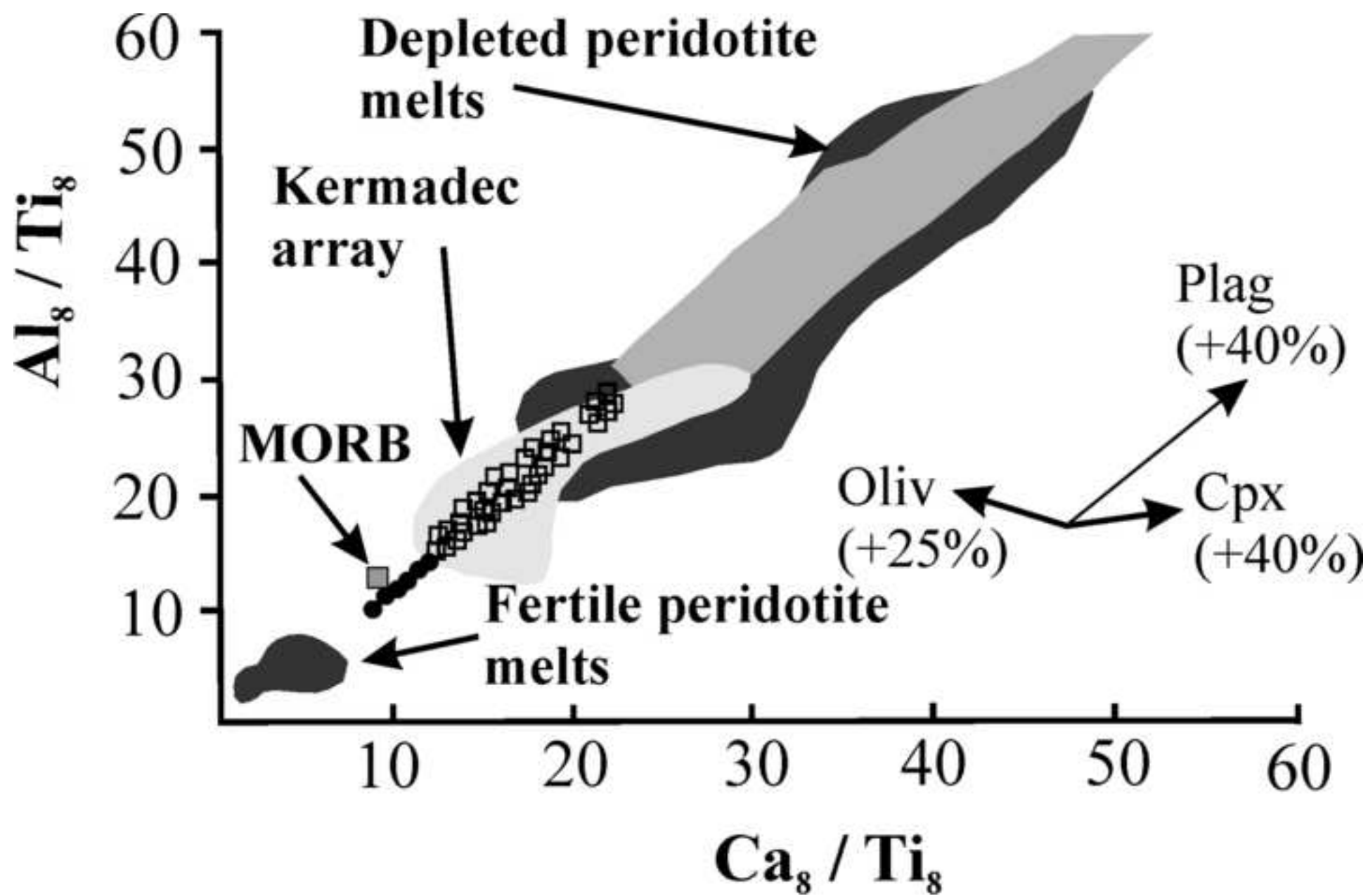


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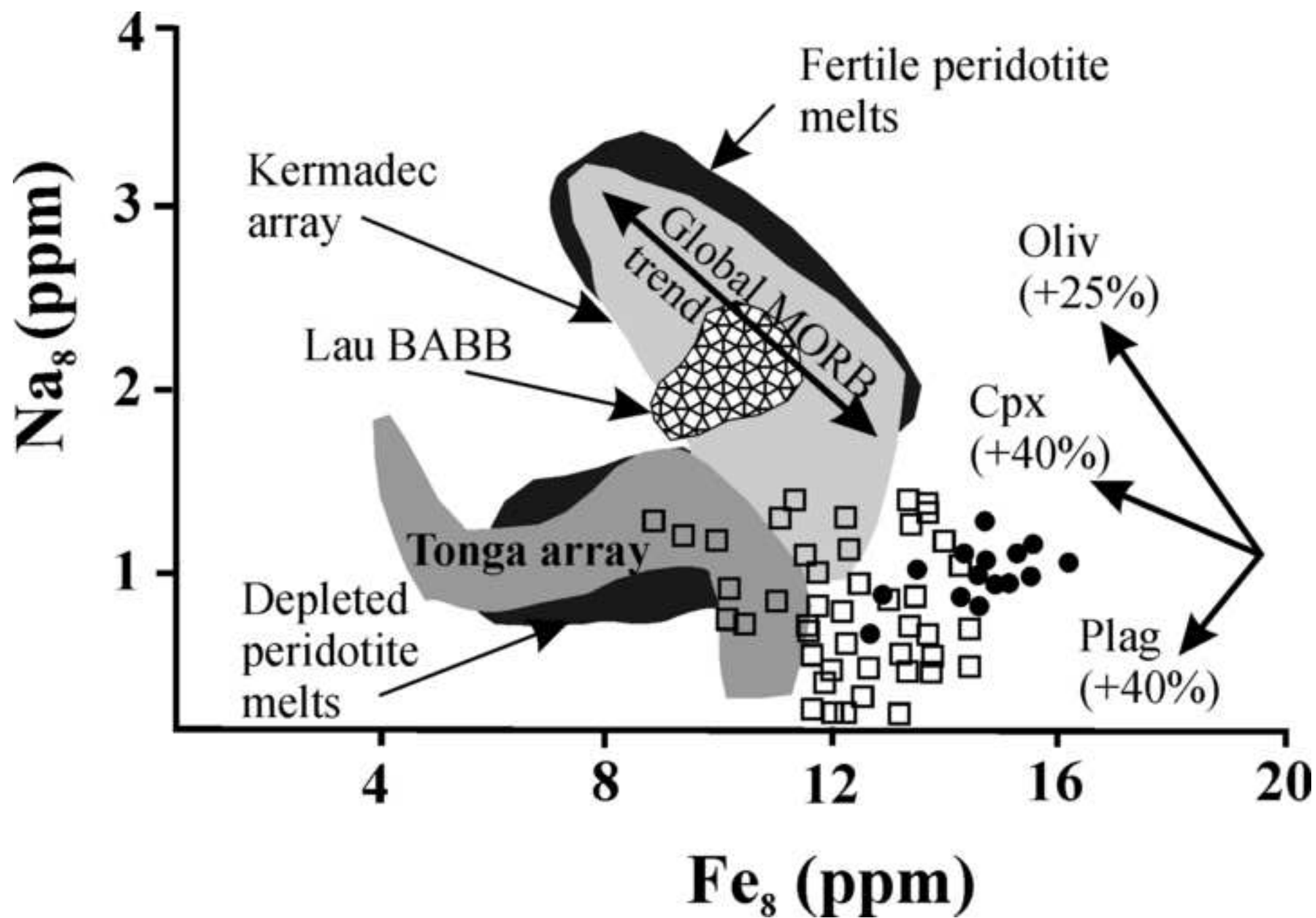
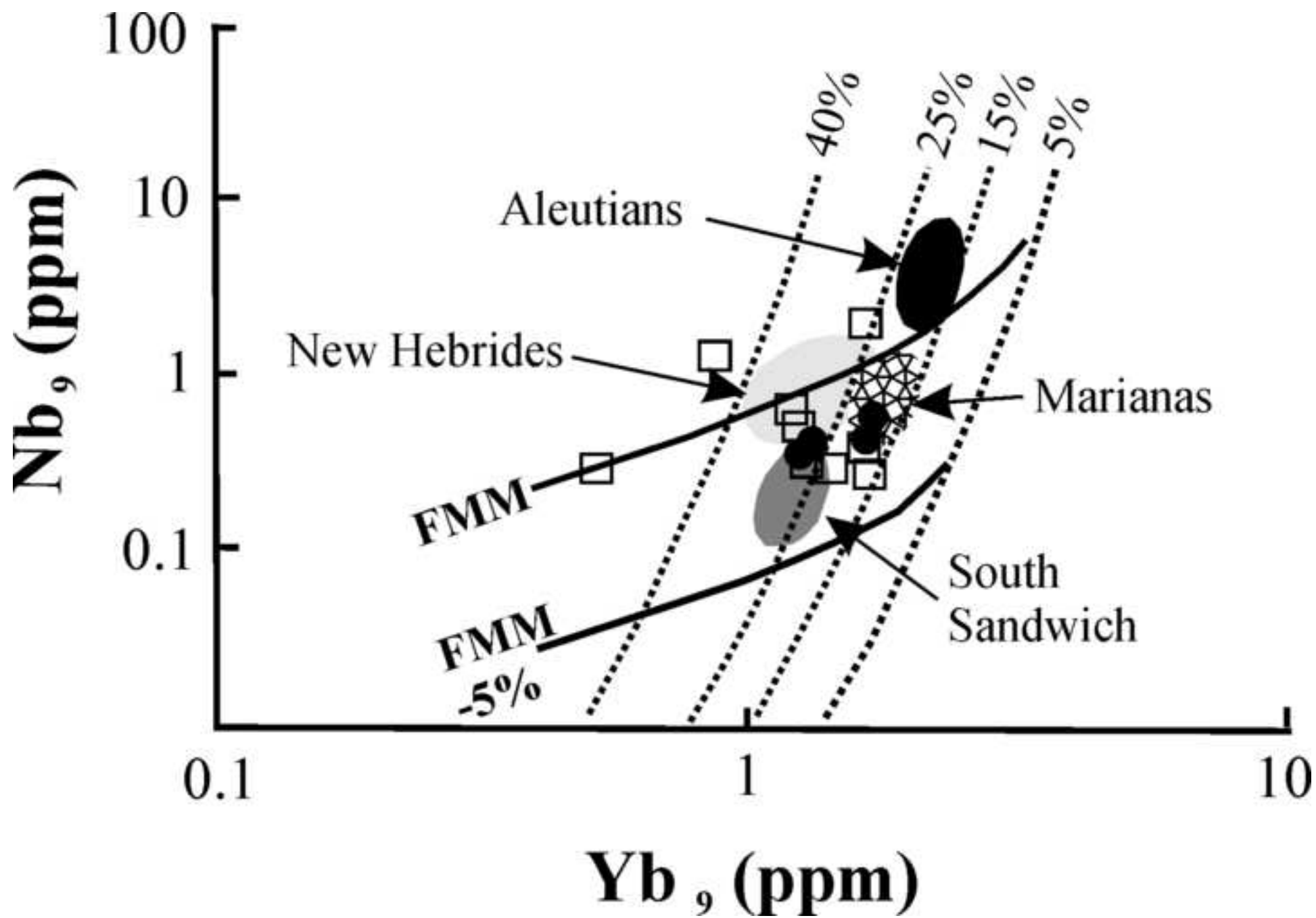
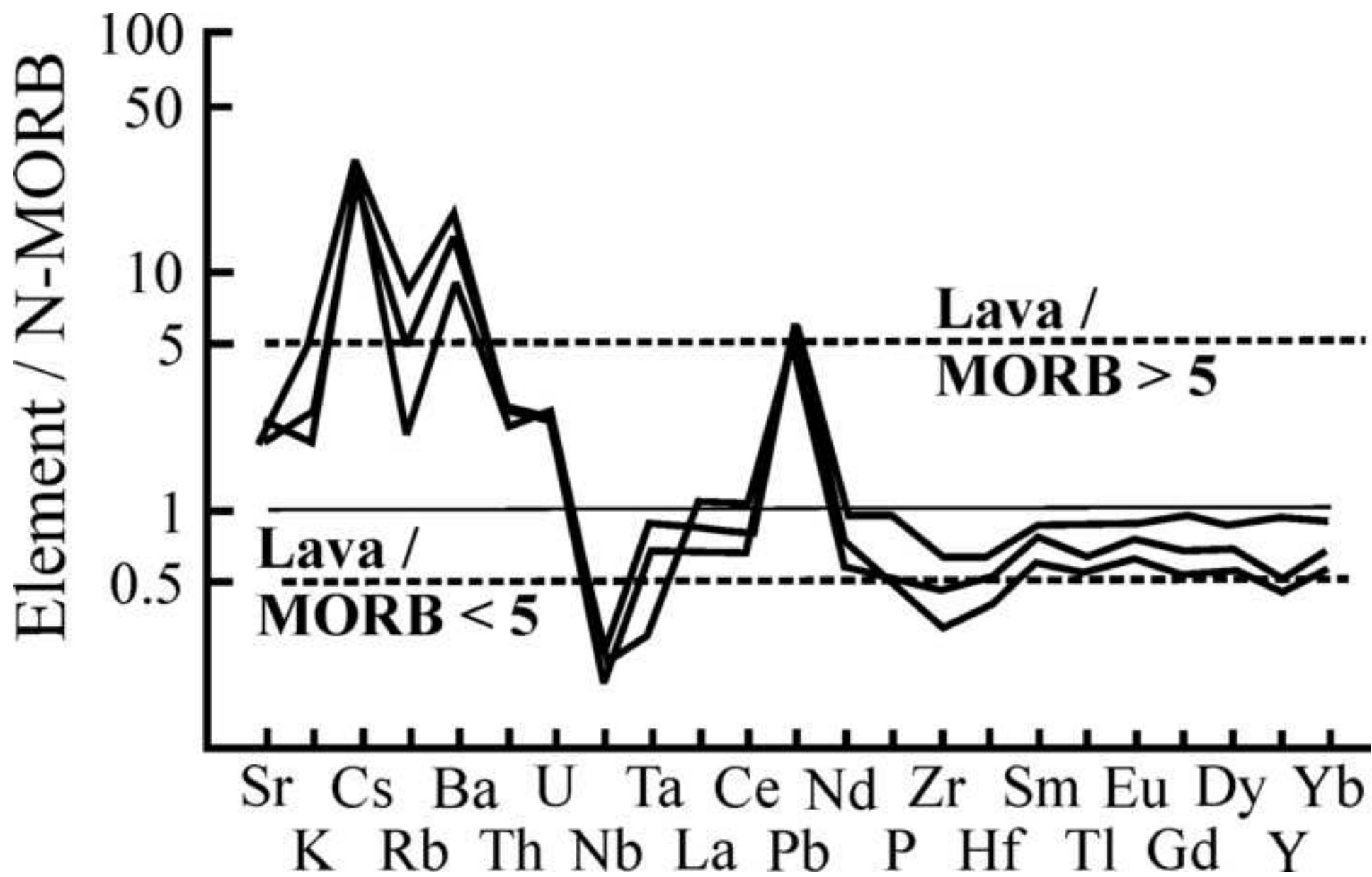


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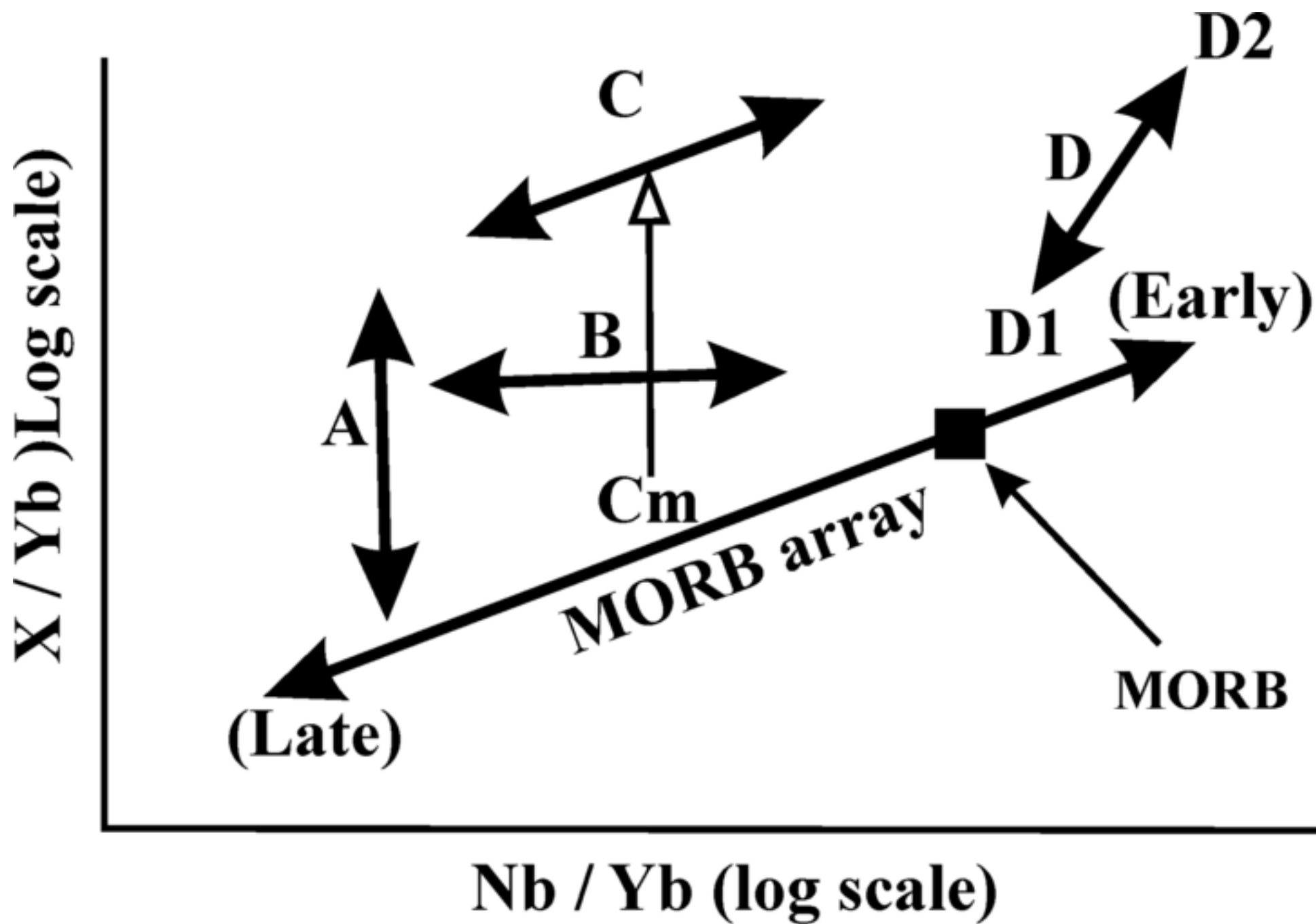


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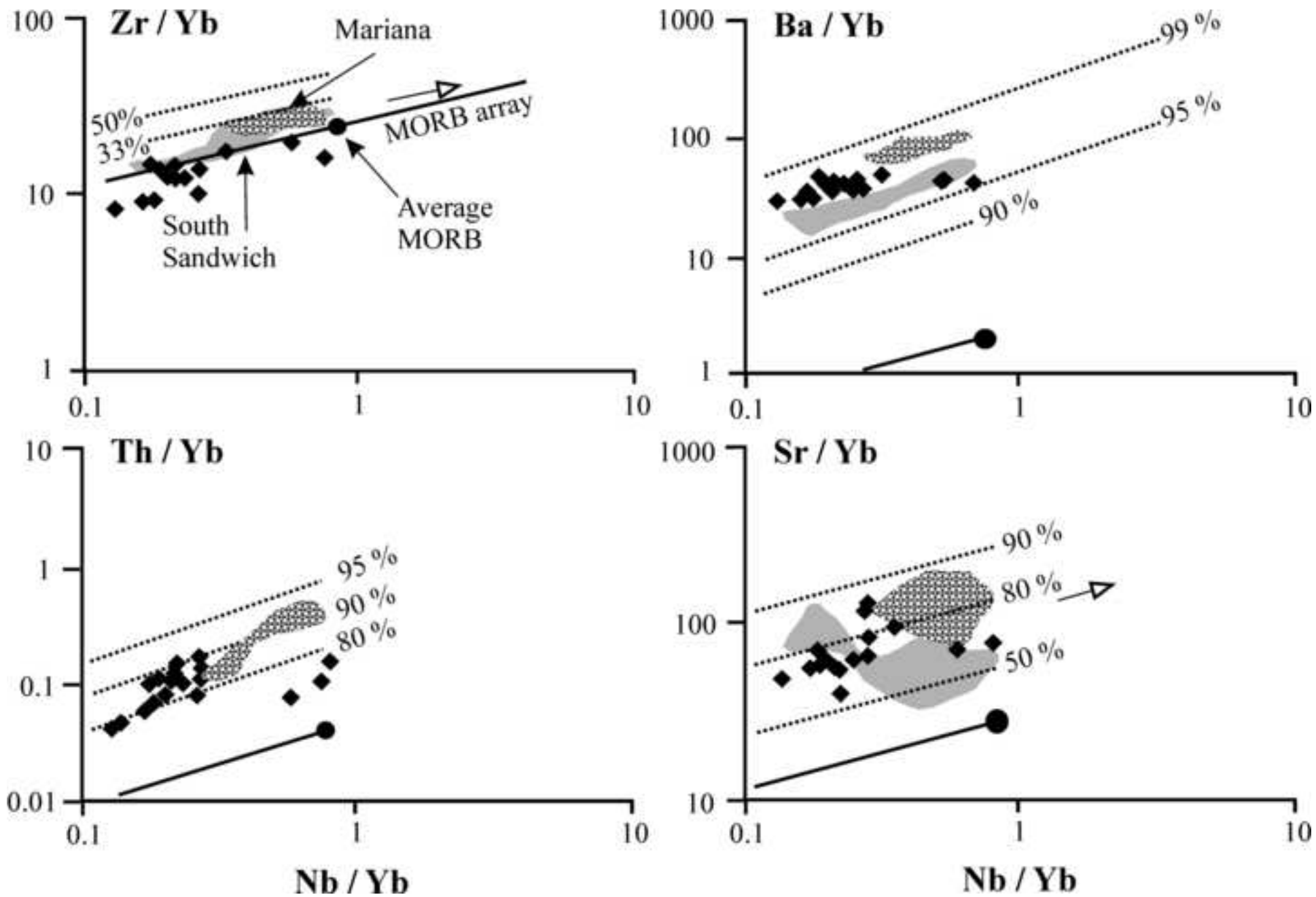


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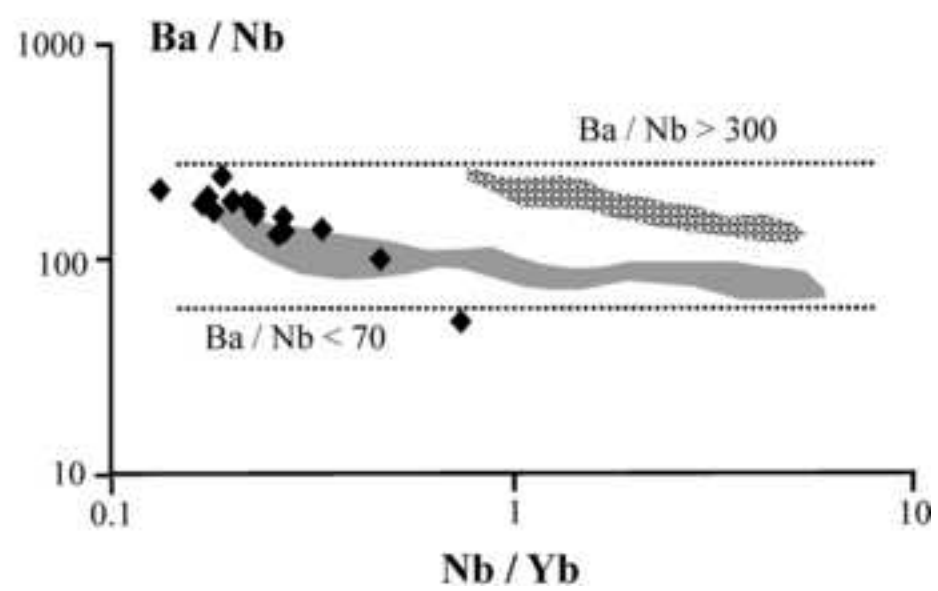
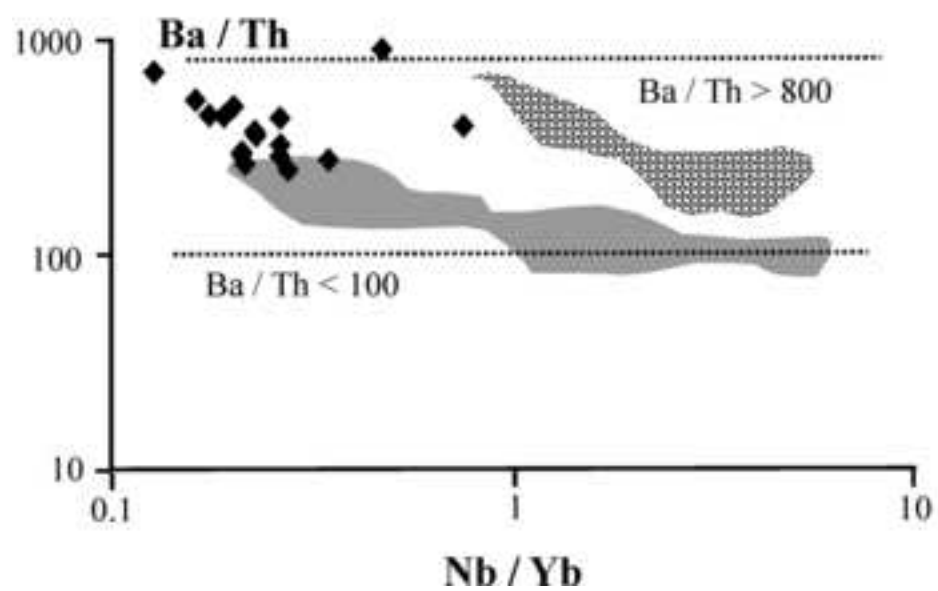
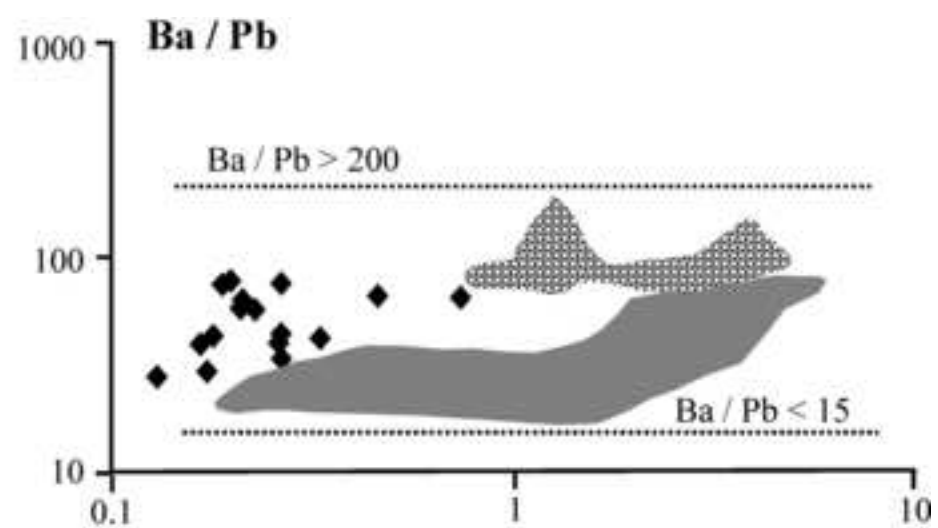
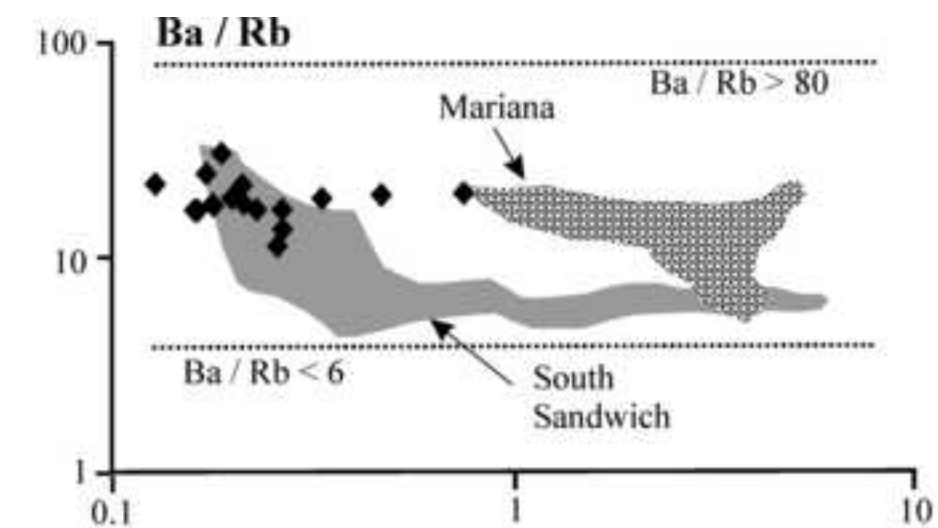
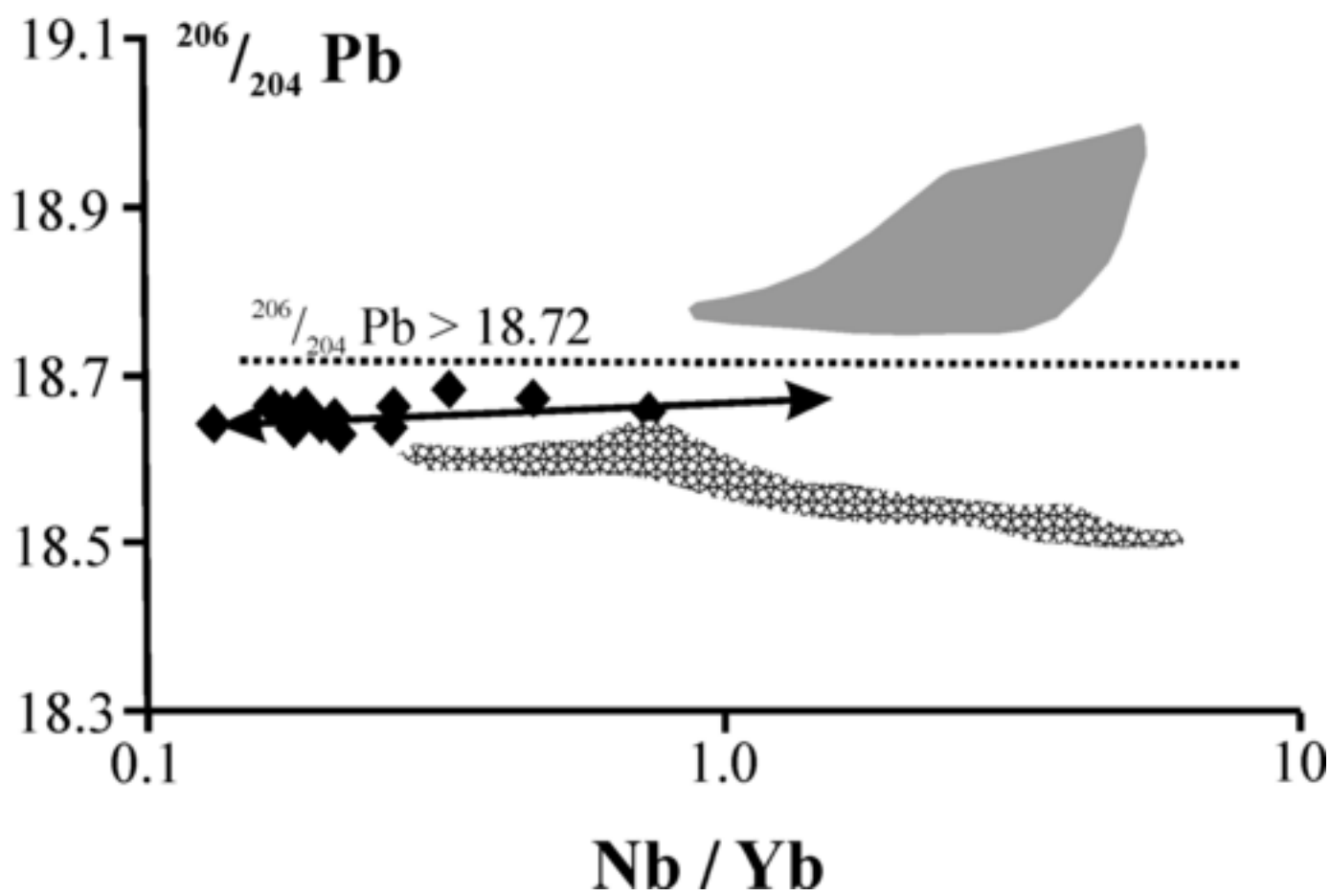
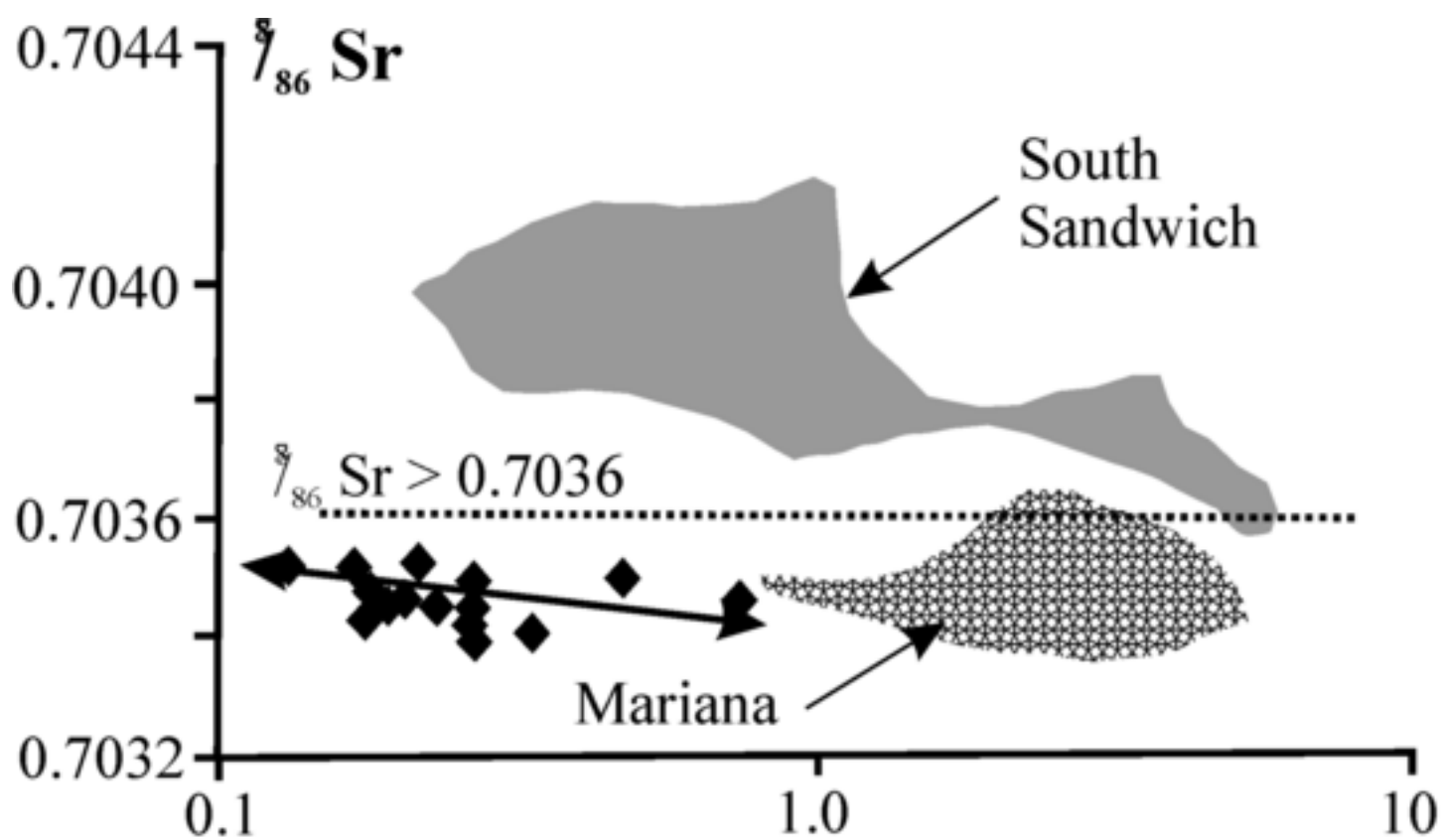


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Table

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AU No.	7135	7114	46357	7125	46329	46330	7144	46325	7148	7090	7053	7096	46362	46358	46368	7088
	45.4	47.4	36.4	37.0	20.6	27.6	37.4	2.8	22.2	aphyric	3.2	27.6	28.8	9.6	18.0	0.6
wt. %																
SiO ₂	47.85	48.84	49.01	49.52	51.44	51.46	51.48	51.67	51.78	53.26	54.83	55.36	55.53	56.50	56.77	57.27
TiO ₂	0.56	0.65	0.75	0.72	0.82	0.92	0.76	1.02	0.66	1.01	1.04	0.72	0.71	0.97	0.70	1.23
Al ₂ O ₃	15.55	20.83	19.17	17.69	18.03	17.28	18.52	15.34	17.72	15.15	14.79	18.10	18.20	15.81	17.53	14.10
Fe ₂ O ₃	1.69	1.58	1.73	1.62	1.76	2.02	1.66	2.17	1.67	2.12	2.09	1.47	1.47	1.81	1.46	2.03
FeO	8.45	7.92	8.63	8.08	8.79	10.11	8.31	10.87	8.36	10.59	10.43	7.35	7.34	9.07	7.31	10.15
MnO	0.18	0.20	0.18	0.19	0.19	0.24	0.19	0.23	0.18	0.25	0.24	0.17	0.18	0.22	0.18	0.23
MgO	10.30	4.61	4.82	6.43	4.61	4.31	4.42	4.95	5.17	4.60	3.72	3.11	3.24	3.55	3.29	2.93
CaO	13.33	12.82	12.18	12.97	11.12	10.45	10.40	10.29	11.22	9.32	8.57	10.18	10.23	8.41	9.59	7.52
Na ₂ O	0.93	1.47	1.60	1.31	1.79	1.90	1.76	1.80	1.71	2.07	2.50	2.08	2.07	2.50	2.04	2.69
K ₂ O	0.11	0.14	0.25	0.18	0.28	0.42	0.13	0.33	0.21	0.34	0.41	0.27	0.26	0.47	0.26	0.62
P ₂ O ₅	0.05	0.06	0.09	0.06	0.10	0.13	0.07	0.10	0.06	0.09	0.11	0.08	0.08	0.14	0.08	0.19
H ₂ O ⁻	0.03	0.03	0.21	0.06	0.12	0.06	0.68	0.10	0.21	0.06	0.22	0.04	0.10	0.06	0.08	0.18
LOI	0.94	0.88	0.96	0.90	0.98	1.13	0.93	1.21	0.93	1.18	1.16	0.82	0.82	1.01	0.81	1.13
Total	99.97	100.04	99.58	99.72	100.03	100.43	99.31	100.09	99.88	100.04	100.11	99.75	100.22	100.52	100.11	100.27
ppm																
Cs	0.11	0.19	0.23	0.19	0.25	0.25	0.14	0.20	0.11	0.30	0.27	0.30	0.36	0.43	0.16	0.36
Ba	49.0	64.3	109.4	85.3	119.6	113.9	139.4	95.4	81.9	102.7	115.6	108.8	104.2	133.8	106.8	168.4
Sr	151.5	209.0	207.0	161.6	216.2	162.7	171.0	141.7	161.9	149.1	161.8	194.2	184.6	186.5	172.6	160.0
Pb	1.21	1.89	2.59	1.95	1.87	1.50	1.91	1.66	2.75	1.76	1.49	2.57	2.58	1.30	3.78	2.71
Th	0.10	0.18	0.37	0.26	0.29	0.41	0.29	0.30	0.22	0.24	0.22	0.22	0.19	0.19	0.15	0.58
U	0.10	0.11	0.17	0.10	0.16	0.11	0.16	0.10	0.10	0.11	0.12	0.14	0.16	n/a	0.18	0.18
Zr	12.7	21.9	37.9	26.0	43.0	34.1	37.4	30.7	33.1	28.4	34.4	30.2	29.0	49.8	28.9	55.7
Nb	0.32	0.42	0.70	0.50	1.99	0.64	0.52	0.53	0.39	0.54	0.55	0.58	0.53	1.42	0.46	0.83
Hf	0.45	0.77	1.55	0.96	1.49	1.32	1.55	1.20	1.39	1.45	1.46	1.33	1.29	1.27	1.22	2.51
Ta	0.16	0.08	0.20	0.11	0.27	0.03	0.13	0.04	0.08	0.04	0.03	0.17	0.09	n/a	0.10	0.06
Y	10.0	12.0	17.3	14.8	24.5	19.3	22.2	20.0	18.1	19.4	21.2	24.7	22.8	25.9	25.3	32.3

Sc	52.6	35.3	36.3	42.9	41.7	31.9	38.9	39.1	40.6	35.8	35.0	33.2	31.4	35.9	32.5	30.9
V	352.7	377.6	350.1	346.8	351.4	335.7	344.2	424.0	334.4	461.4	365.8	307.3	296.5	301.5	279.1	268.2
Cr	227.6	17.5	45.6	137.7	40.2	12.0	28.4	19.6	25.6	17.8	24.0	15.7	18.1	15.4	16.6	5.8
Co	54.4	35.4	42.6	40.2	40.2	32.9	34.6	34.1	38.3	31.8	27.3	29.0	27.9	26.1	27.2	25.3
Ni	97.9	25.3	36.8	58.3	33.9	19.1	23.9	17.7	28.4	17.8	16.6	20.2	19.3	13.1	19.7	7.4
Cu	73.4	81.2	147.5	84.3	140.1	96.6	102.2	178.6	143.8	142.1	113.1	140.8	74.4	86.1	64.6	102.2
Zn	50.5	55.8	66.3	59.7	67.9	65.1	66.2	67.1	60.8	68.1	73.6	67.8	66.1	76.2	67.3	81.5
Ga	10.6	13.6	14.3	12.7	18.1	12.2	13.6	11.6	12.9	11.9	12.4	13.9	13.7	16.1	13.5	13.1
Ge	0.45	0.44	0.69	0.80	0.91	0.60	0.57	0.57	0.57	0.60	0.59	0.60	0.57	1.13	0.54	0.81
La	1.29	1.54	3.31	1.96	3.07	3.25	2.34	2.49	1.70	2.35	2.71	2.60	2.61	2.65	2.48	4.54
Ce	3.85	4.53	9.03	5.66	8.68	8.71	6.33	7.00	5.18	6.69	7.66	7.75	7.61	7.52	7.34	11.99
Pr	0.68	0.80	1.46	0.97	1.47	1.47	1.25	1.18	0.92	1.17	1.34	1.41	1.36	1.17	1.34	2.11
Nd	3.34	4.11	7.48	5.07	7.72	7.70	6.44	6.26	5.08	5.98	6.95	7.28	7.35	6.95	7.55	11.26
Sm	1.27	1.44	2.54	1.76	2.63	2.46	2.41	2.17	1.82	2.21	2.50	2.77	2.73	2.21	2.75	3.81
Eu	0.48	0.57	0.93	0.70	1.02	0.87	0.91	0.81	0.73	0.88	0.98	0.99	1.10	0.82	1.07	1.28
Gd	1.51	1.76	2.84	2.30	3.45	3.13	3.18	3.05	2.60	3.05	3.12	3.56	3.35	2.86	3.67	5.11
Tb	0.27	0.33	0.51	0.40	0.60	0.51	0.52	0.46	0.42	0.41	0.52	0.68	0.71	0.56	0.70	0.74
Dy	1.89	2.28	3.22	2.85	3.96	3.49	3.84	3.41	3.07	3.08	3.98	4.72	4.60	3.99	4.80	5.35
Ho	0.42	0.49	0.73	0.59	0.91	0.79	0.84	0.77	0.70	0.72	0.92	1.02	0.99	0.80	1.08	1.27
Er	1.13	1.48	1.98	1.58	2.31	2.05	2.25	2.07	1.85	1.89	2.41	2.86	2.78	2.15	3.02	3.19
Tm	0.18	0.22	0.31	0.25	0.42	0.38	0.41	0.39	0.32	0.38	0.41	0.45	0.40	0.40	0.41	0.67
Yb	1.24	1.57	2.11	1.87	2.67	2.41	2.74	2.51	2.25	2.32	2.76	3.24	3.18	2.53	3.53	3.87
Lu	0.16	0.20	0.33	0.22	0.41	0.34	0.34	0.33	0.29	0.37	0.38	0.44	0.45	0.39	0.48	0.55
⁸⁷ Sr/ ⁸⁶ Sr	0.70342	0.70349	0.70341	0.70340	0.70347	0.70345	0.70346	0.70353	0.70343	0.70345	0.70346	0.70347	0.70352	0.70349	0.70352	0.70353
¹⁴³ Nd/ ¹⁴⁴ Nd	0.51306	0.51305	0.51303	0.51305	0.51304	0.51304	0.51305	0.51305	0.51305	0.51304	0.51304	0.51305	0.51307	0.51305	0.51305	0.51303
²⁰⁶ Pb/ ²⁰⁴ Pb	18.648	18.662	18.685	18.639	18.652	18.656	18.656	18.647	18.659		18.643	18.646	18.667	18.656	18.641	18.636
²⁰⁷ Pb/ ²⁰⁴ Pb	15.571	15.558	15.577	15.563	15.566	15.556	15.565	15.555	15.571		15.546	15.556	15.574	15.559	15.565	15.555
²⁰⁸ Pb/ ²⁰⁴ Pb	38.342	38.316	38.371	38.343	38.333	38.305	38.316	38.286	38.387		38.268	38.332	38.356	38.320	38.319	38.288

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Element vs. MgO	Slope	Intercept	r ²
SiO ₂	-3.216	68.866	0.86
TiO ₂	0.043	0.863	0.05
Al ₂ O ₃	0.12	14.399	0.06
FeO	1.13	5.692	0.57
CaO	1.109	4.285	0.92
Na ₂ O	-0.341	3.696	0.81
K ₂ O	-0.058	0.652	0.21

Table

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Element	Raoul		South	Mariana	Ruapehu
	range	average	Sandwich average	average	(basalt)
Zr	<20%	5%	10%	25%	5%
Nd	20-40%	30%	30%	40%	35%
La	50-60 %	55%	55%	65%	55%
Sr	70-80 %	75%	80%	82%	65%
Th	80-90 %	85%	90%	90%	90%
K	80-95 %	90%	87%	92%	80%
Pb	91-97 %	95%	95%	92%	92%
Rb	95-97 %	96%	96%	96%	96%
Ba	96-98%	98%	96%	98%	96%
Cs	99->99%	99%	99%	99%	98%

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	Subduction cm/year	Backarc extension cm/year	Basin width km	Nb/Yb range	Nb/Yb average
Raoul South	8.1	2.1	130	0.13-0.33	0.22
Sandwich Central	7.5	6.5	250	0.14-0.76	0.34
Mariana	7.7	3	240	0.28-0.72	0.49

Table

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	Raoul		South Sandwich	Mariana
Subduction cm/yr)	8.1		7.5	7.7
Crust (age)	Jurassic		27-80 Ma	Jurassic
Sediment (m)	100-150		200-400	300-500
Data source:	DSDP595/596	DSDP204		
Ba (g/yr/arc-cm)	145	38	95	140
Rb(g/yr/arc-cm)	3.4	5.3	7.6	12.1
Th (g/yr/arc-cm)	0.84	0.73	0.69	1.02
K(g/yr/arc-cm)	1490	2130	1990	3610
Sr (g/yr/arc-cm)	20	16	44	35
La (g/yr/arc-cm)	11.4	5.4	1.7	6.2
$^{87}\text{Sr}/^{86}\text{Sr}$	0.7095	0.7075	0.7087	0.7062
$^{206}\text{Pb}/^{204}\text{Pb}$	18.76	18.81	18.64	18.92